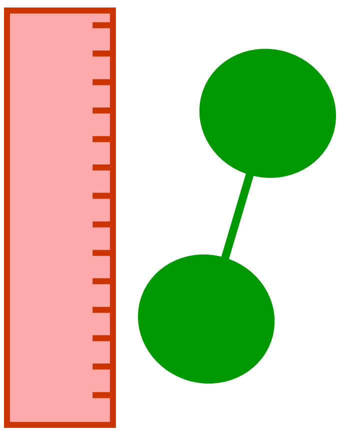
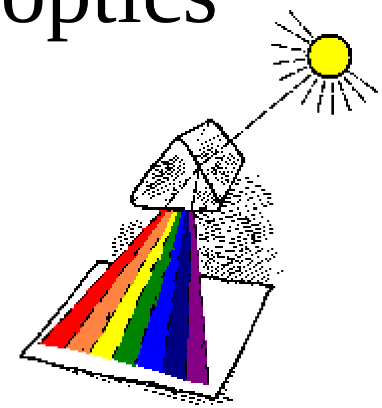
Control of External Molecular Modes:

Molecular alignment & Molecular optics





In intense laser fields

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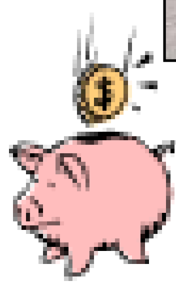
Northwestern University

NORTHWESTERN UNIVERSITY

Thanks to:

$ NSF CHE/DMR
$ NSF PHY
$ DOE
$ NATO
$ HGF-NRC
$ Guggenheim Foundation
$ Humboldt Foundation



NORTHWESTERN UNIVERSITY

OUTLINE

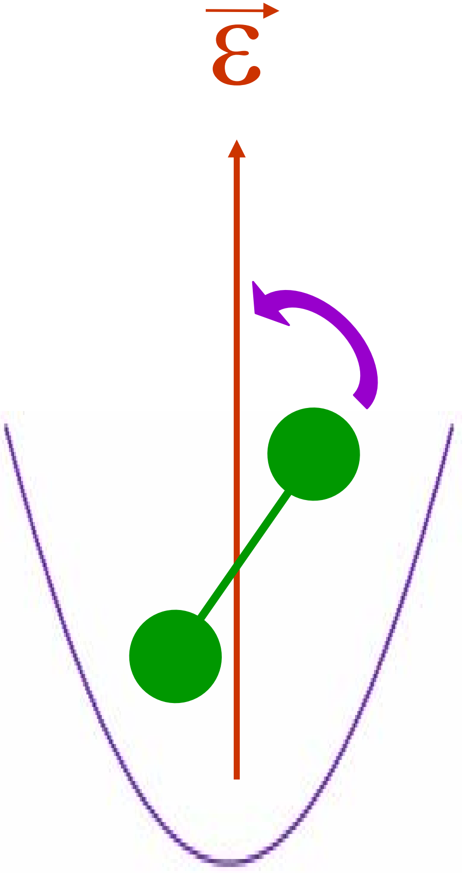
- Alignment in intense laser fields
is easy to understand classically

- Enhanced alignment after the pulse turn-off
is a pretty quantum interference effect

- Three-dimensional alignment

- Molecular optics:
focusing, collimating, guiding & dispersing
molecular beams with light

$$mR_e^2\,\ddot{\theta} = -\frac{\partial}{\partial\theta} V[\,\theta\,;\,\vec{\varepsilon}\,]$$



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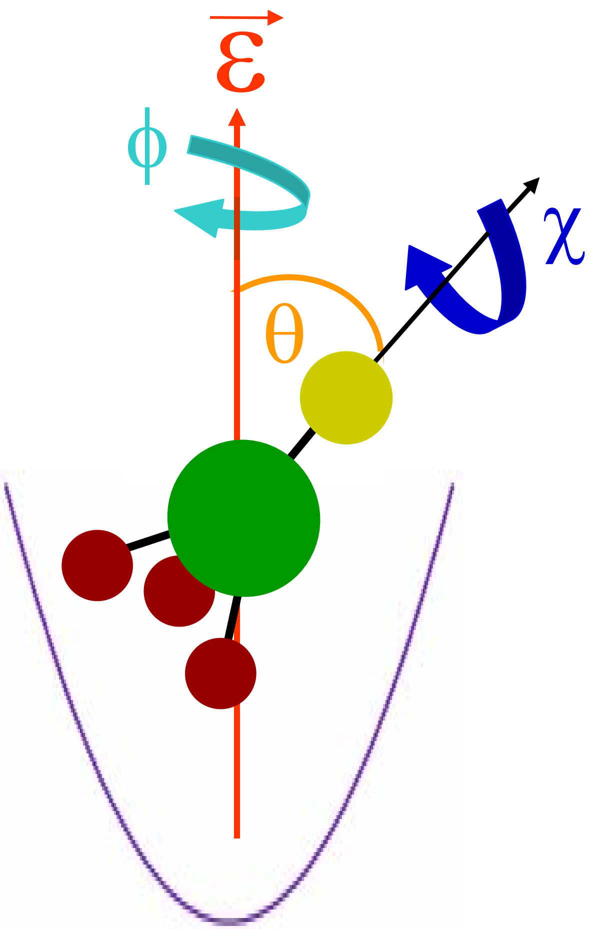
Alignment is a one-dimensional concept

θ confined

χ free

ϕ free



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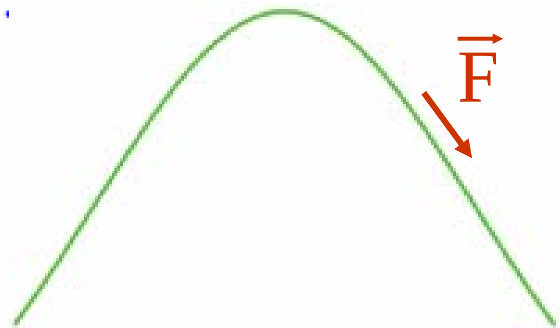
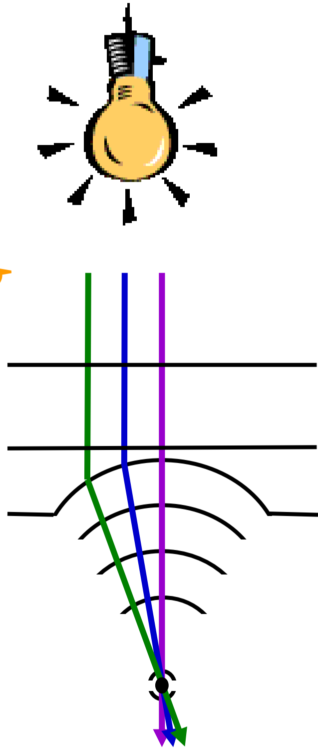
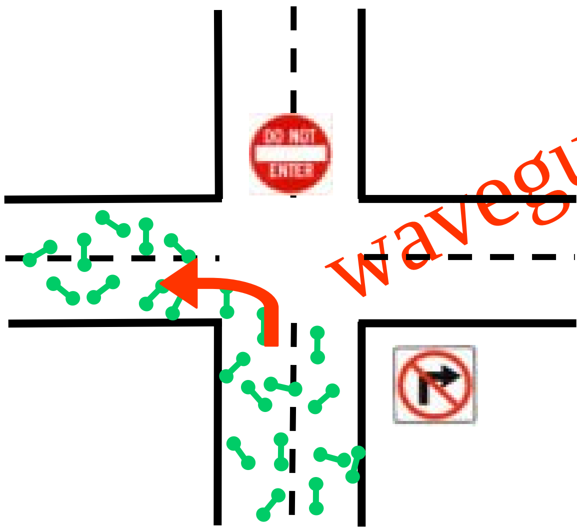


$I \propto \exp(-R^2/\omega_0^2)$

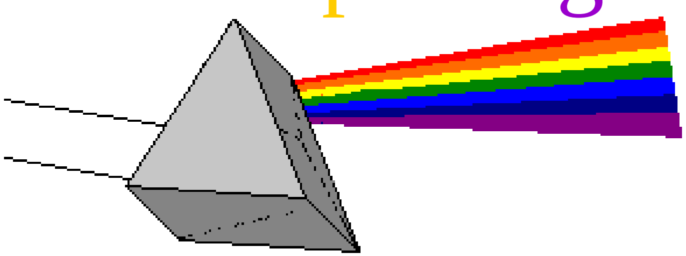
focusing



waveguiding



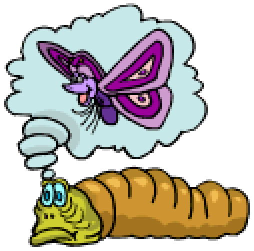
dispersing



reflecting

cont.

- Repulsive optical elements
- Simultaneous alignment & focusing– field free
- Applications:
  - -Time-resolution of nonradiative transitions
  - -Nanolithography
  - -Generations of attosecond pulses
  - -Control of photoreaction branching ratios
  - -New forms of electron diffraction
- Few of my favorite dreams

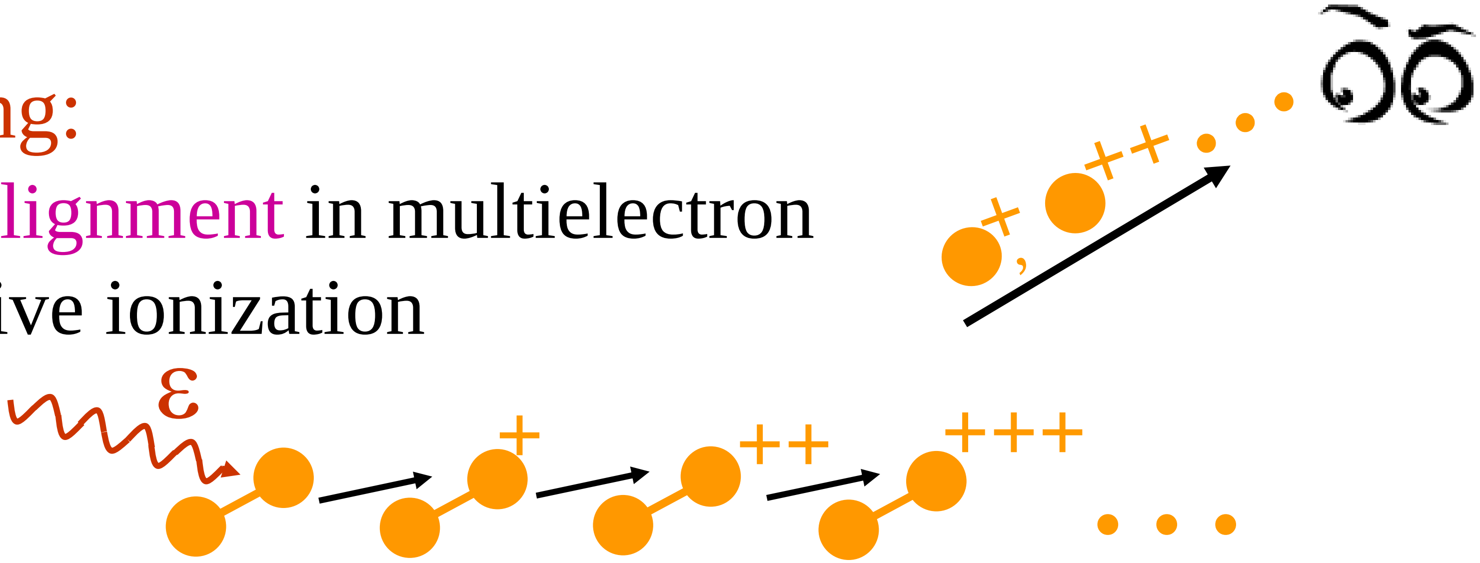


  - -Control of solution dynamics
  - -Alignment & optics in superfluids

Laser alignment is a simple but general phenomenon:

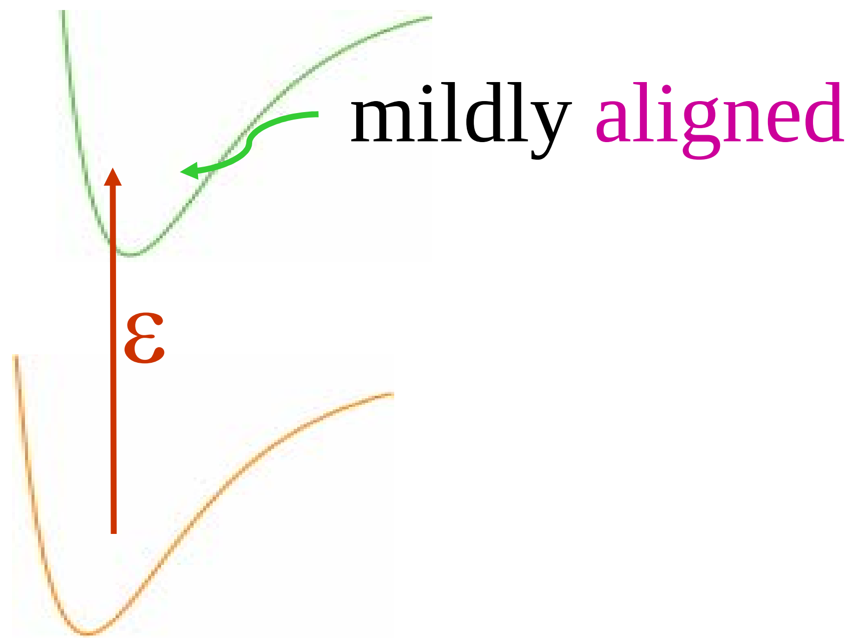
ε = strong:

Role of alignment in multielectron dissociative ionization



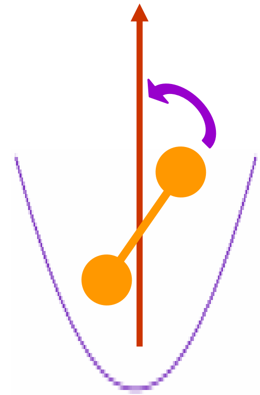
$\varepsilon \longrightarrow 0$:

Optical polarization of excited states:

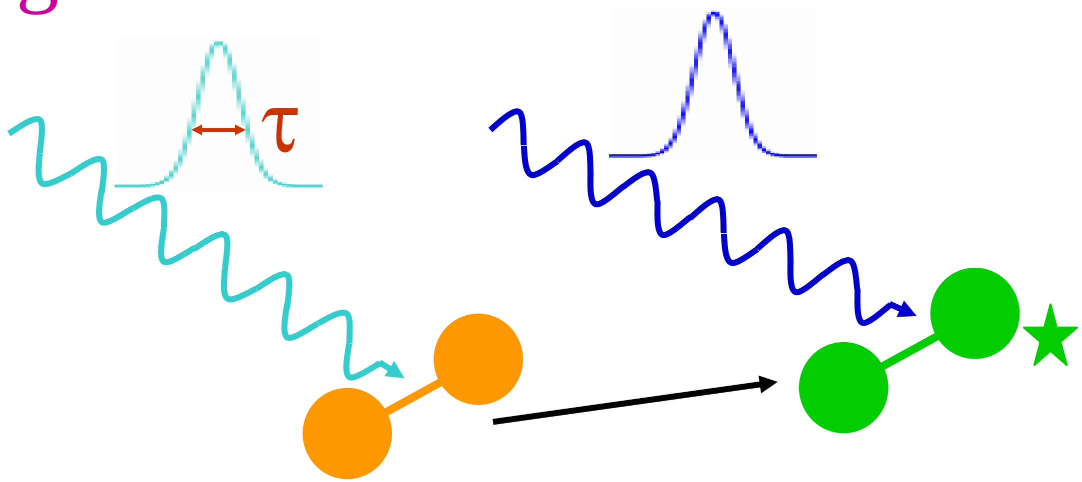


$\tau \rightarrow \infty$ Alignment in a strong DC field

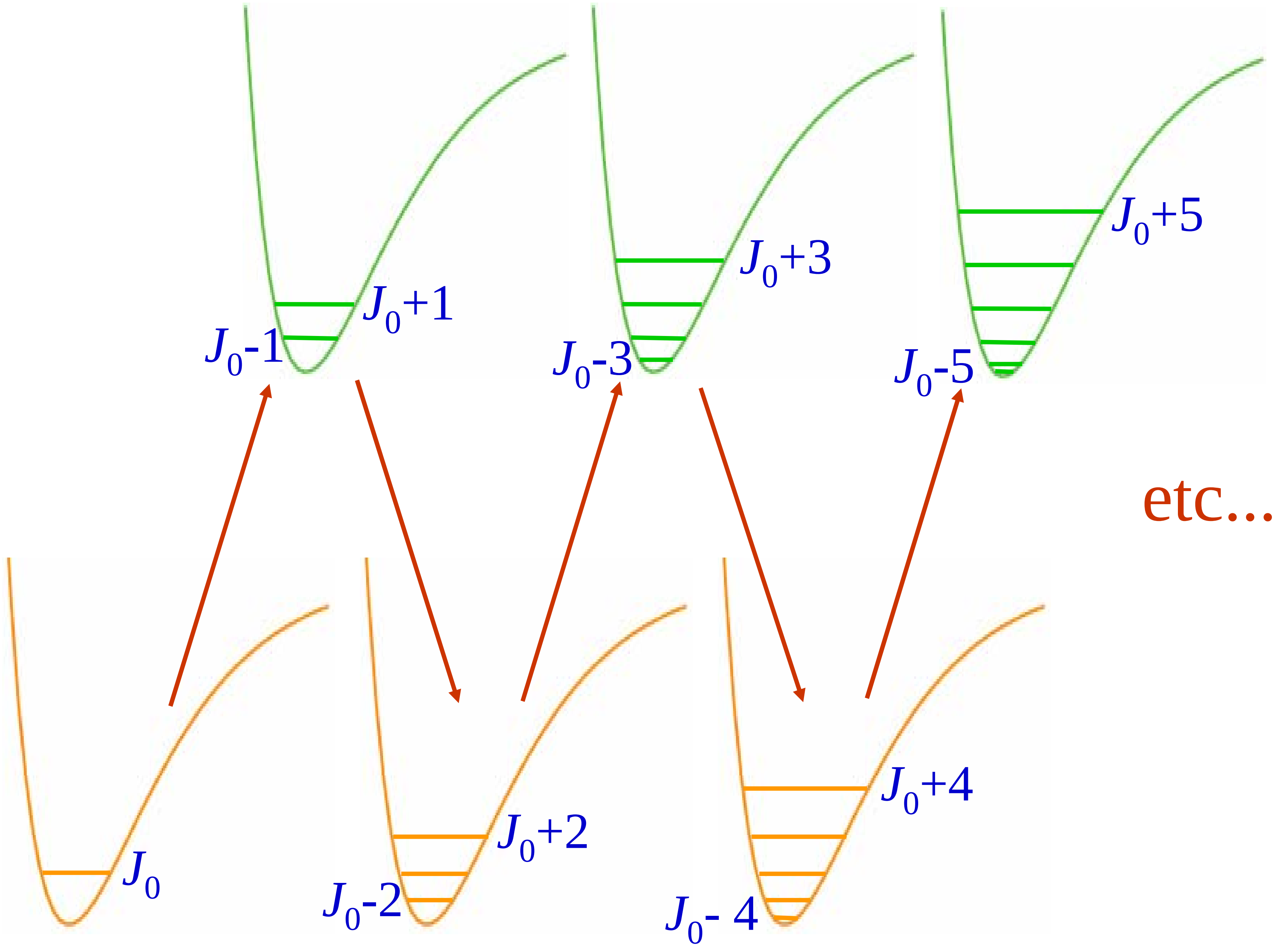
$\vec{\varepsilon}$ = static



τ = short: Dynamical alignment in pump-probe experiments



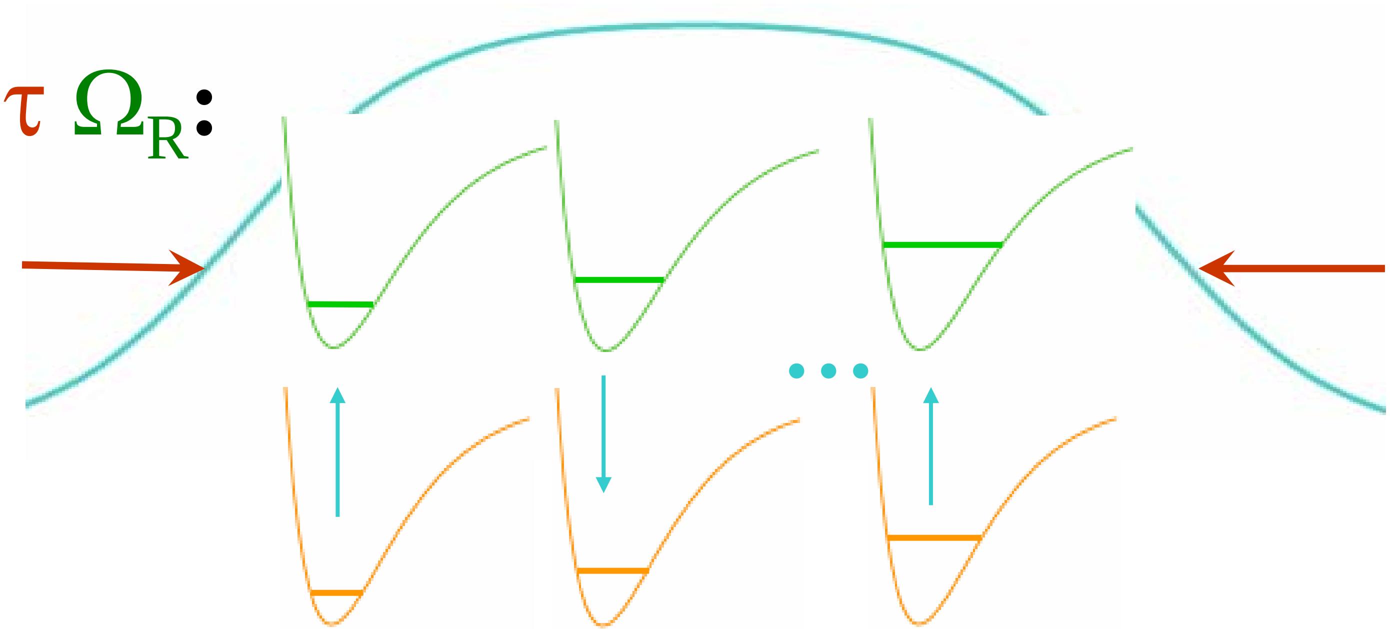
$\varepsilon \rightarrow 0$ Rotational coherence spectroscopy



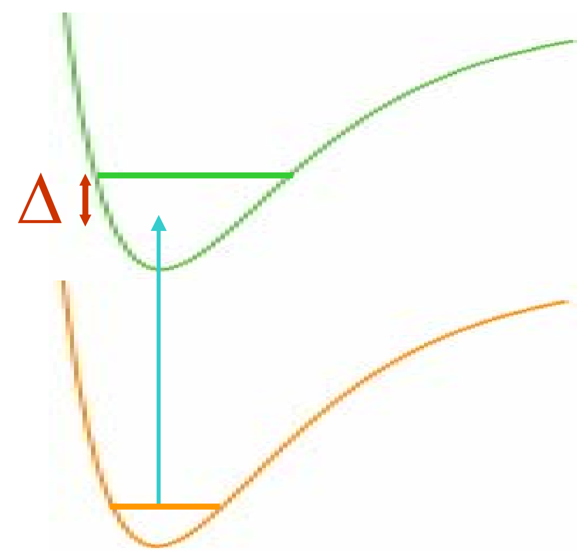
T.S., J.Chem.Phys. **103**, 7887 (1995)

What terminates the rotational excitation?

Either $J_{max} \sim \tau\, \Omega_R$:

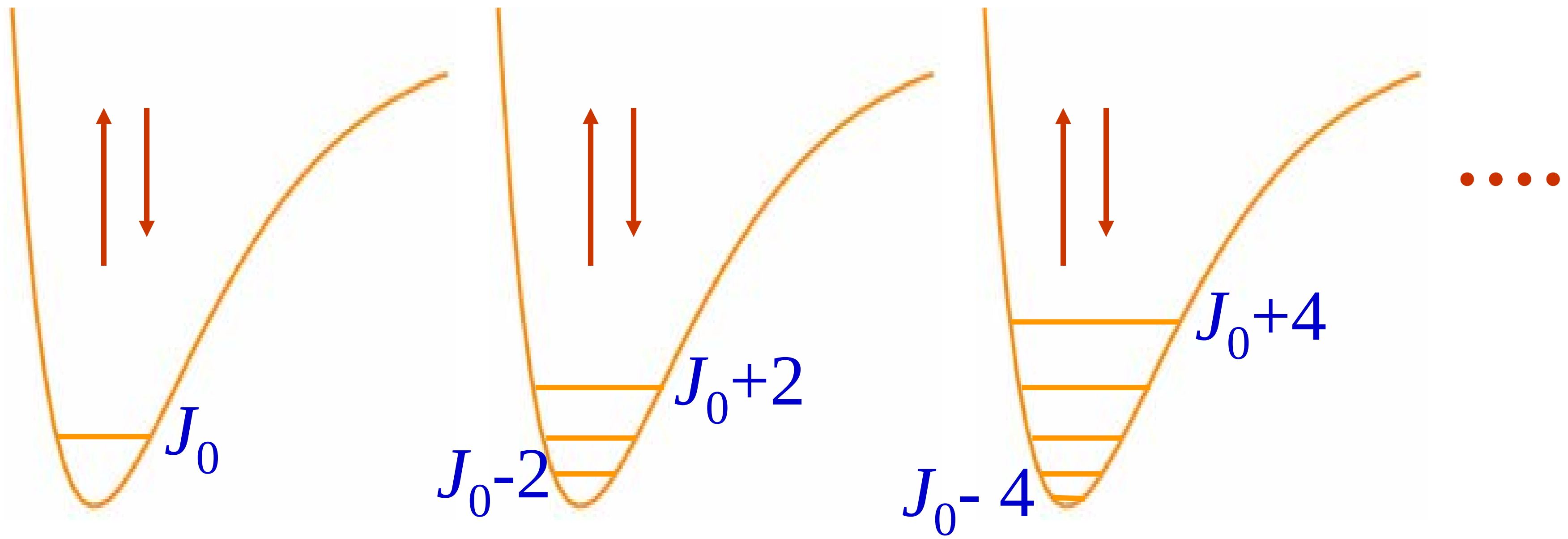


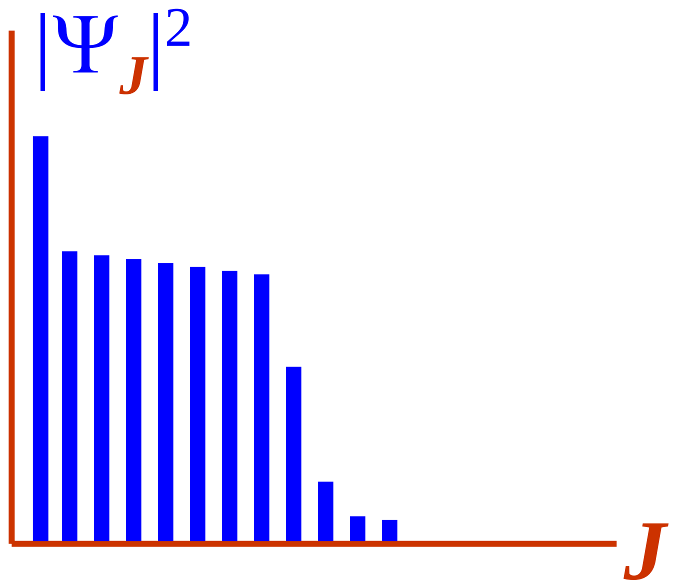
Or $\Omega_R \sim \Delta(J_{max})$:



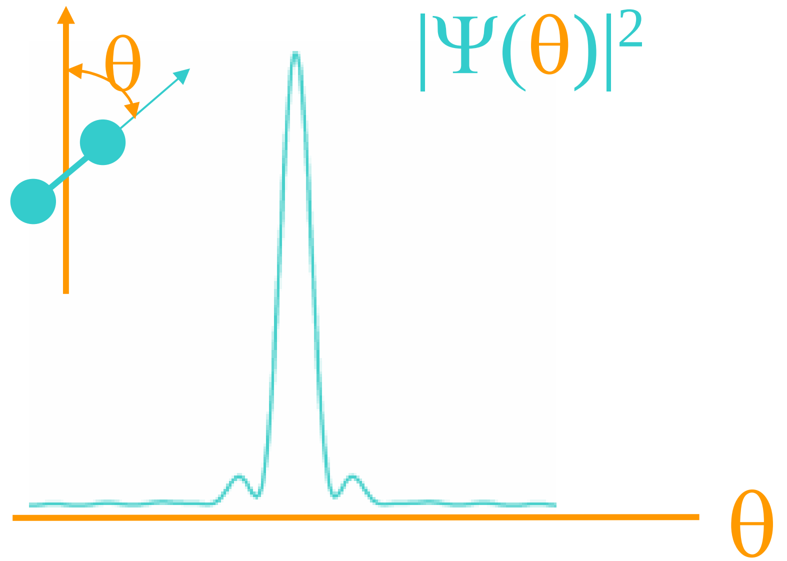
$$[\ \Delta(J) \sim B_e J(J+1)\ ]$$

At nonresonant frequencies ($\omega << \omega_{elect}$) rotational excitation takes place via two-photon cycles



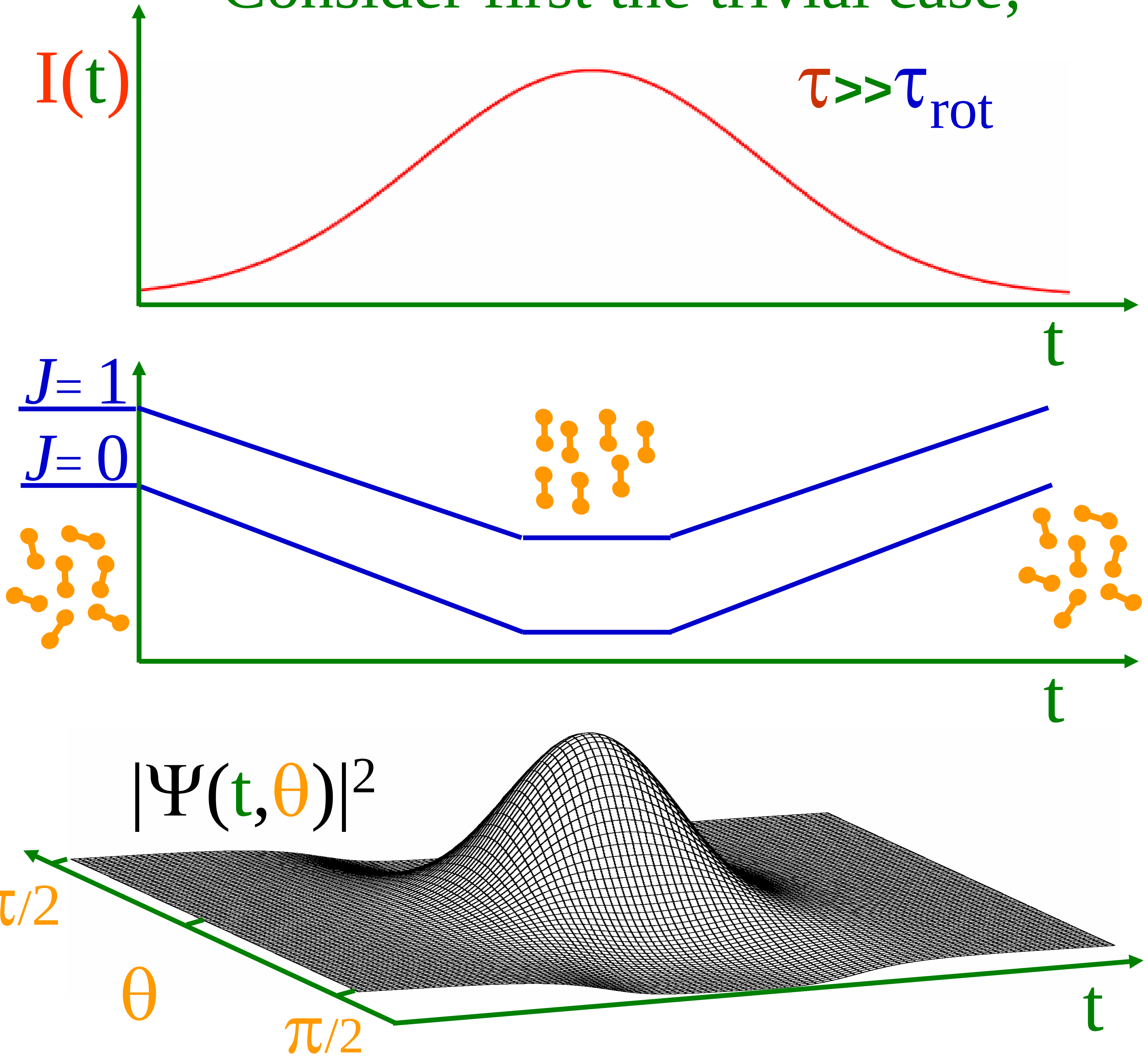


$$\Delta J \Delta \theta \gtrsim 1$$

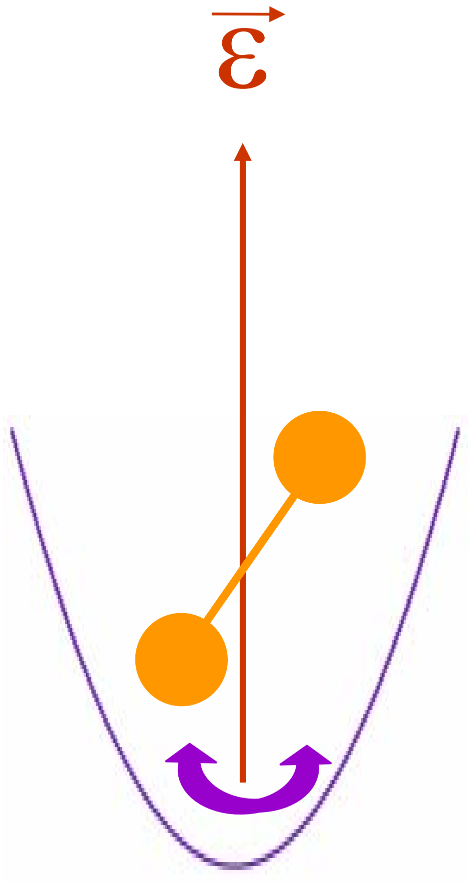


But in principle alignment is not guaranteed

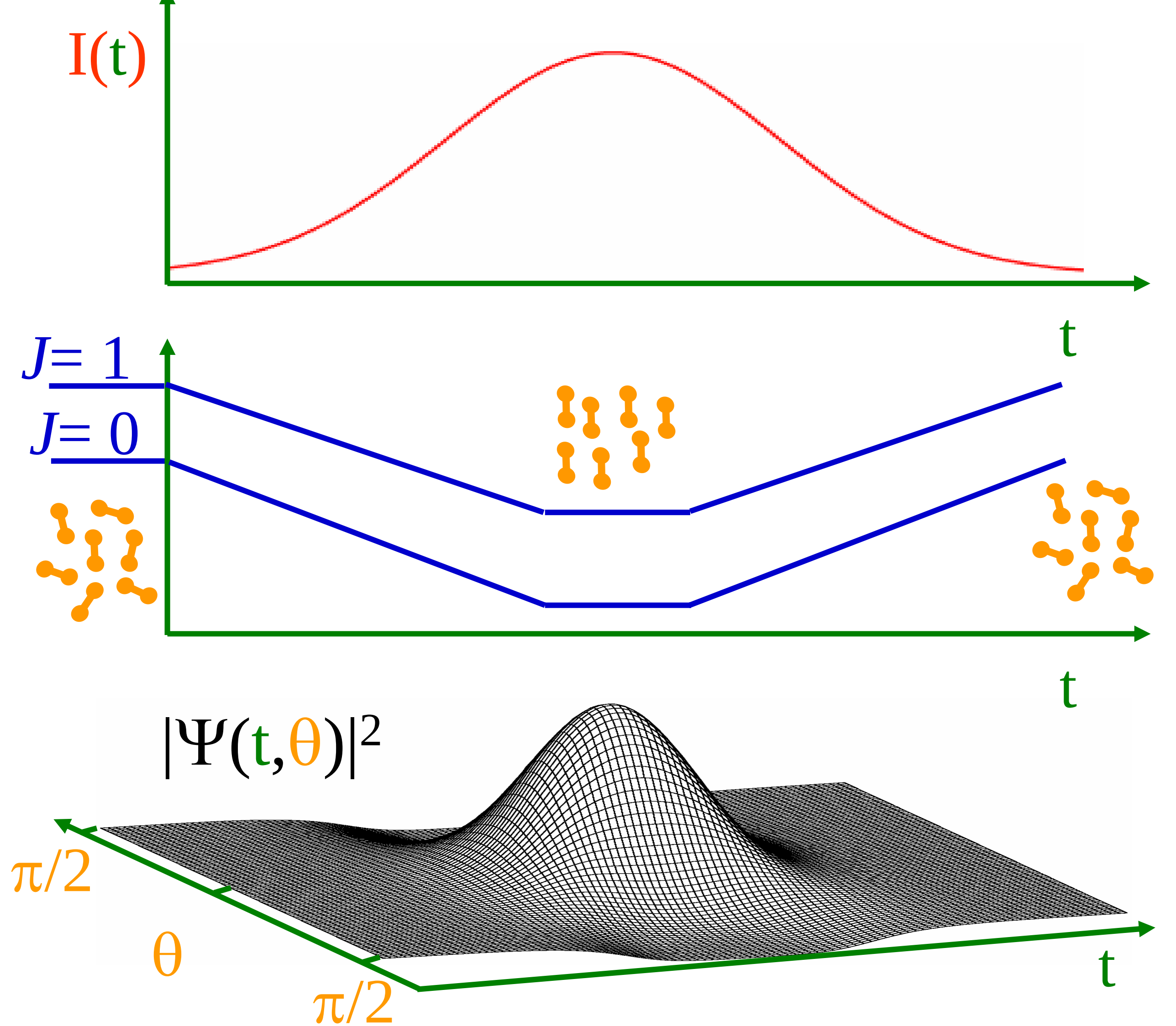
Consider first the trivial case;



In the long pulse limit laser alignment converges to alignment in a strong DC field



Static (adiabatic) alignment, $\tau \gg \tau_{rot}$



Zon & Katsnel'son, JETP 42, 595 (1976)

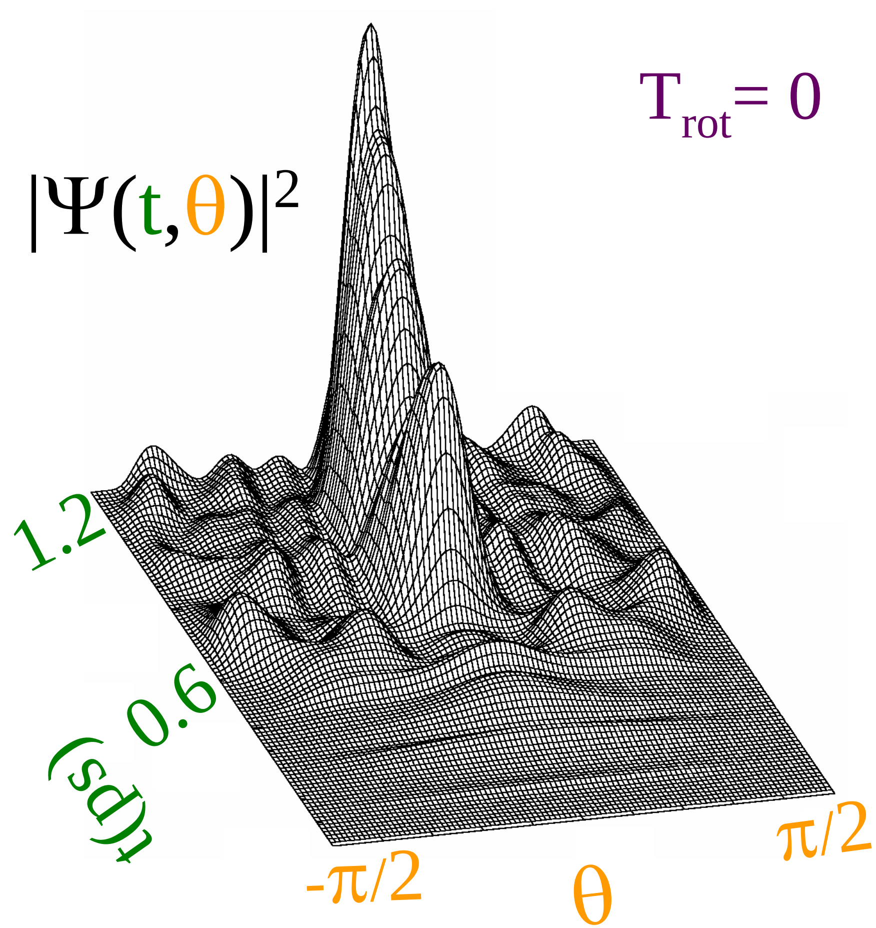
Friedrich & Herschbach, Phys.Rev.Lett. 74, 4623 (1995)

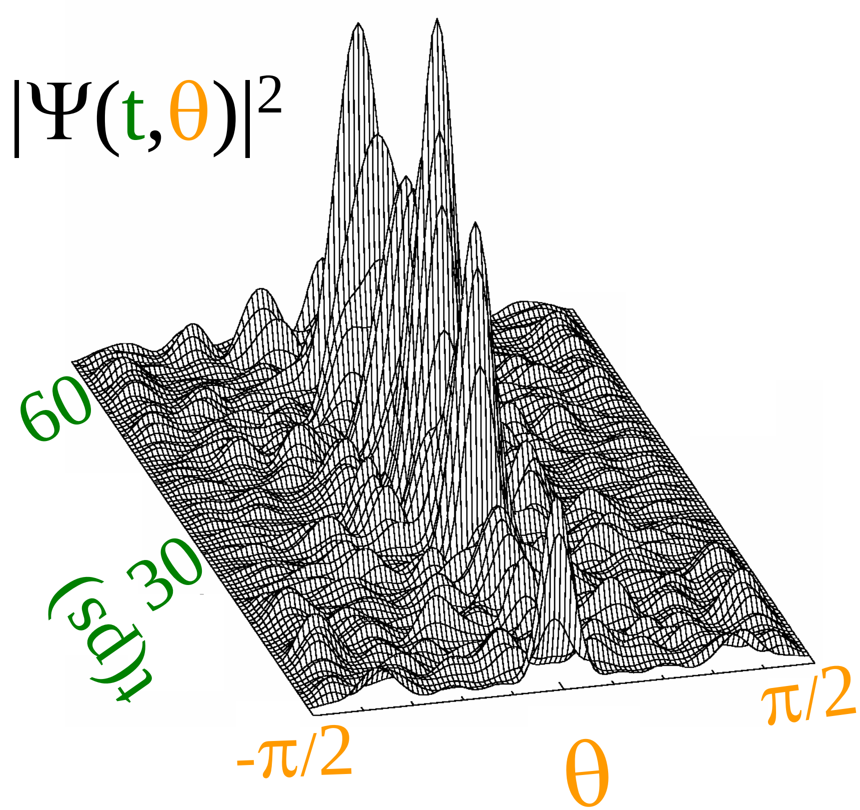
Kim & Felker, J.Chem.Phys. 104, 1147 (1996)

Laren *et al*, J.Chem.Phys. 109, 8857 (1998)

Dynamical alignment during a τ=200 fs pulse

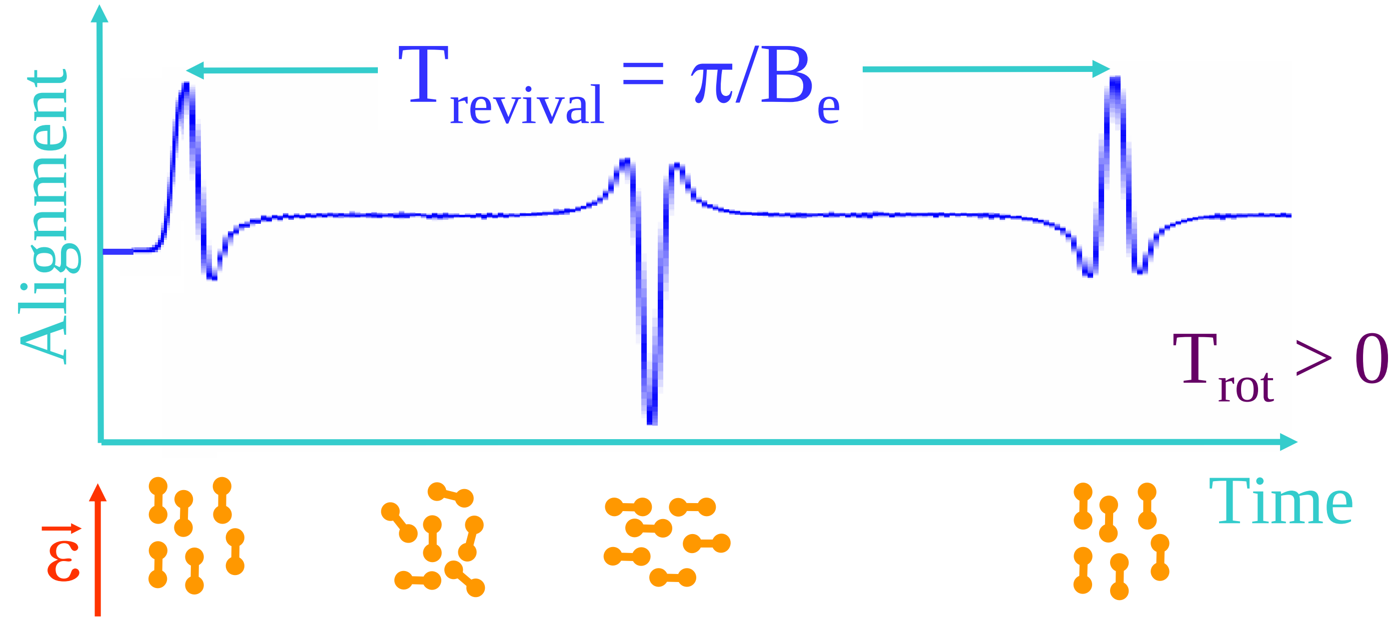
Alignment is enhanced after the turn off





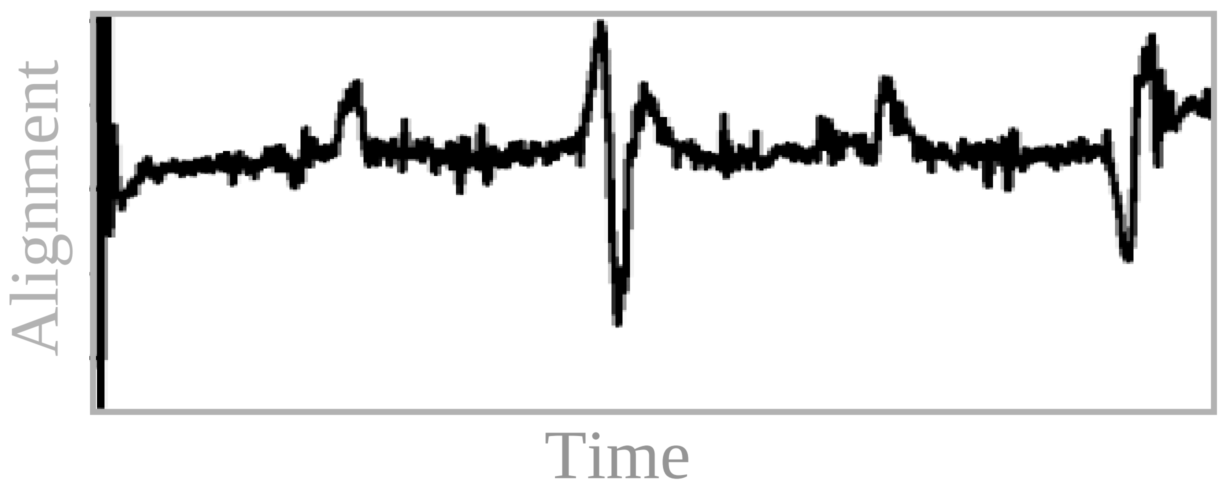
T.S., Phys.Rev.Lett. **83**, 4971 (1999)

Theory:



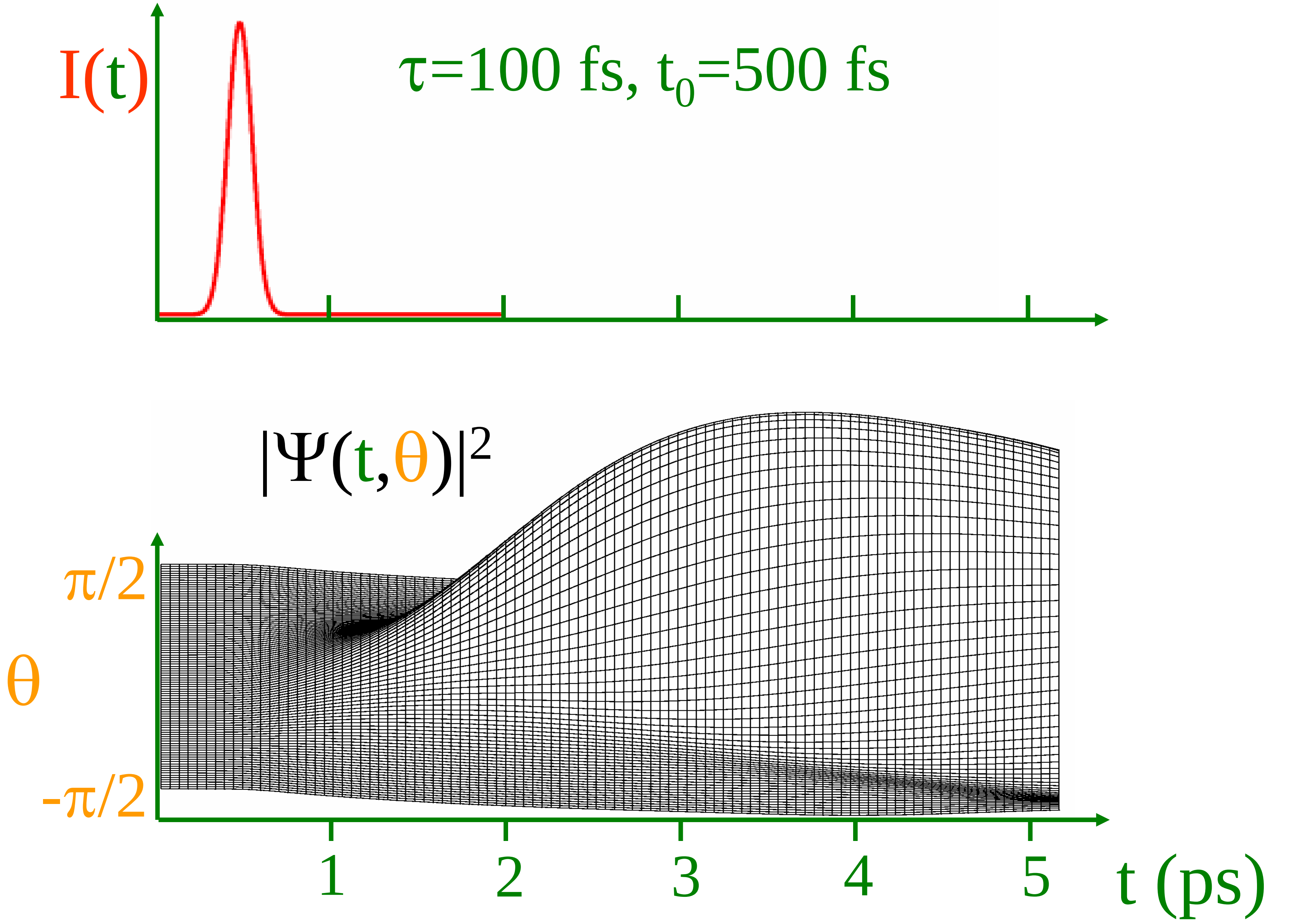
T.S., Phys.Rev.Lett. **83**, 4971 (1999)

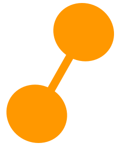
A recent experimental demonstration:

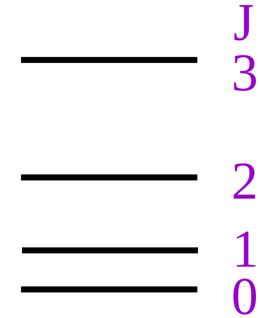


F. Rosca-Pruna & M.J.J. Vrakking, Phys.Rev.Lett **87**, 153902 (2002)

In the impulse ($\tau \ll \tau_{rot}$) limit the dynamics simplifies again

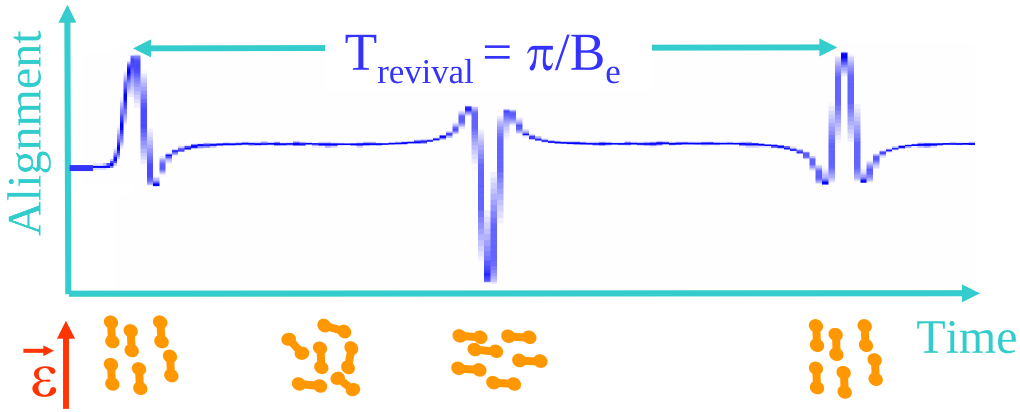


Linear rotors  have simple rotational spectra:

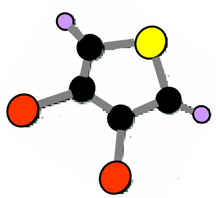


$E_J = BJ(J+1)$

and hence simple rotational revival dynamics:

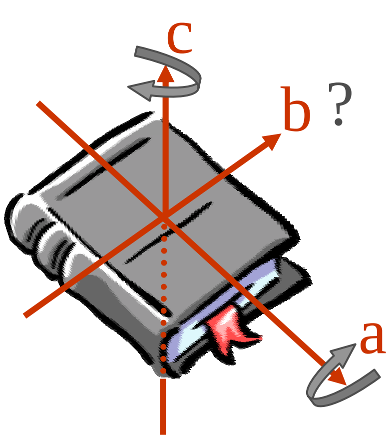


$$\dot{\theta} = 0, \quad \dot{\phi} = J/I$$

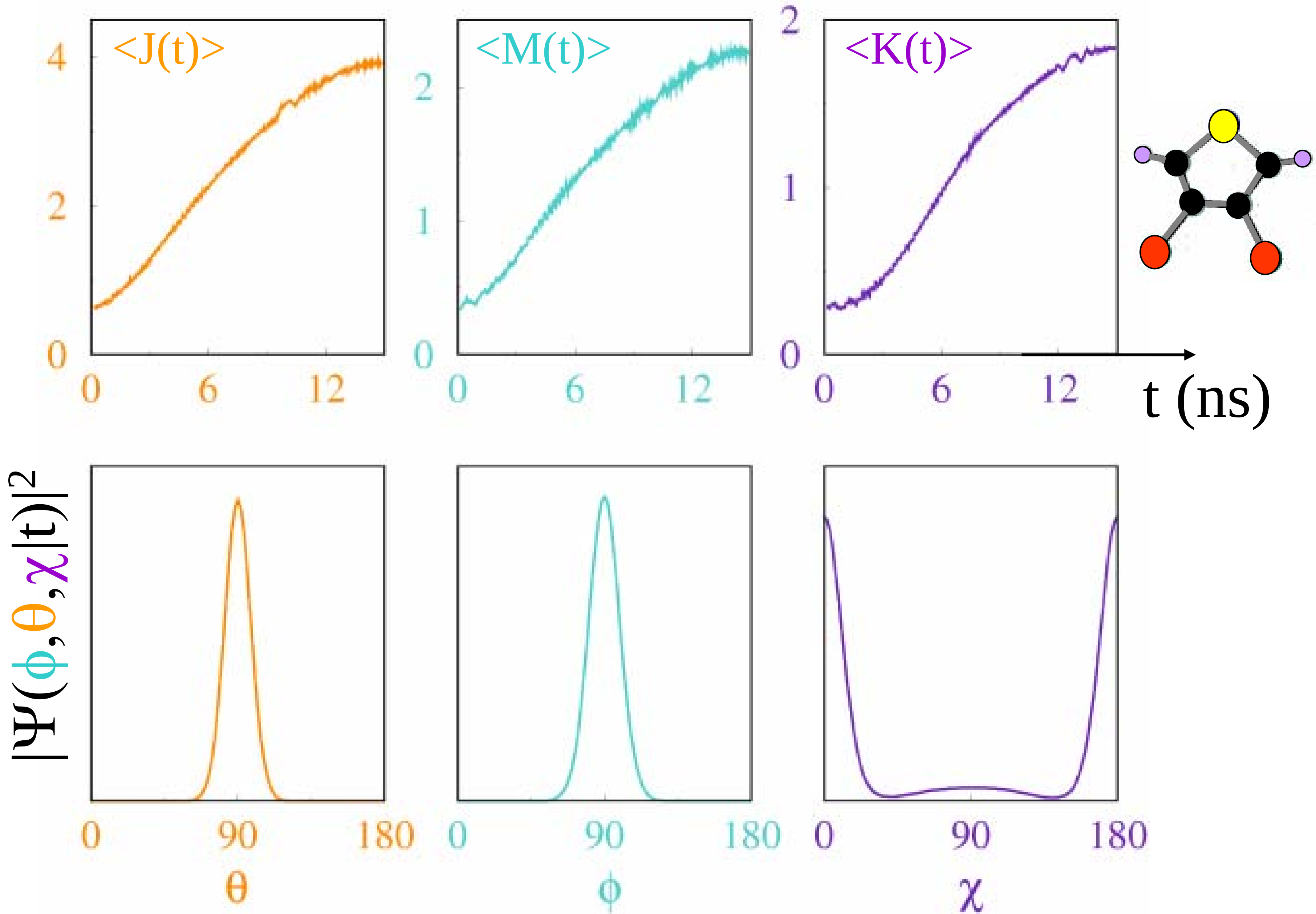
But molecules  are more interesting than that

(most of them are asymmetric tops)

$$2E_{J\tau} = (A+C)J(J+1) + (A-C)E_{J\tau}(\kappa)$$



Revival Structure of Asymmetric Top Molecules: Theory & Experiments, Phys.Rev.Lett., **91**, 043003 (2003)



Phys.Rev.Lett. **85**, 2470 (2000)

Epilogue

Moderately intense laser fields excite rotations via sequential 1-photon cycles (at $\omega \sim \omega_{elec}$) ,

$$i\dot{C}_J(t) = E_J C_J(t) - \Sigma_{J'} (J \mid \mu \cdot \varepsilon(t) \mid J') \, C_{J'}(t),$$

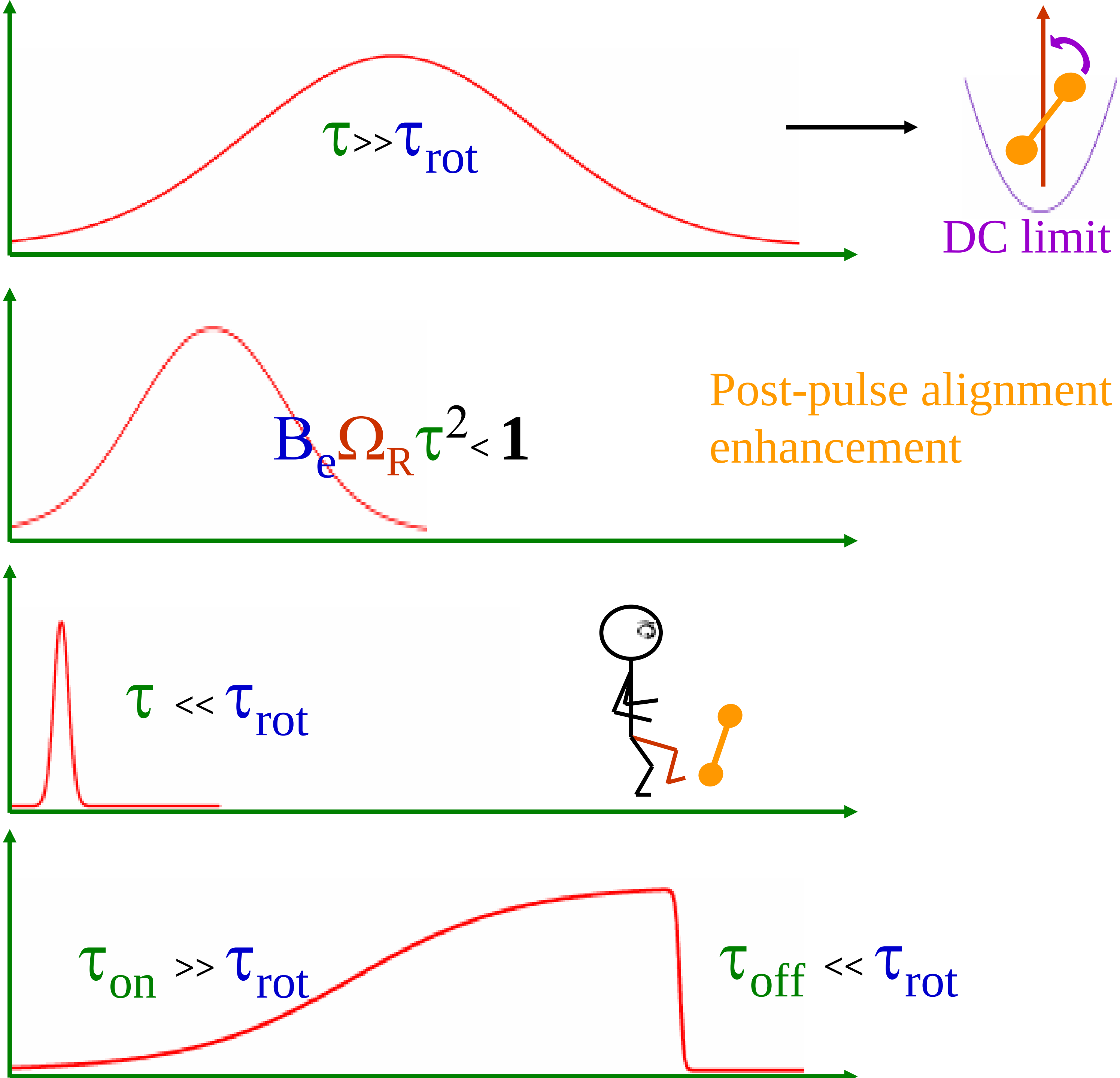
or via 2-photon cycles (at $\omega \ll \omega_{elect}$),

$$i\dot{C}_J(t) = E_J C_J(t) - \frac{\varepsilon^2(t)}{4} \Sigma_{J'} (J \mid \beta \mid J') \, C_{J'}(t).$$

The resulting wavepacket,

$$\Psi(\theta,t) = \Sigma_J C_J(t) \, \phi_J(\theta),$$

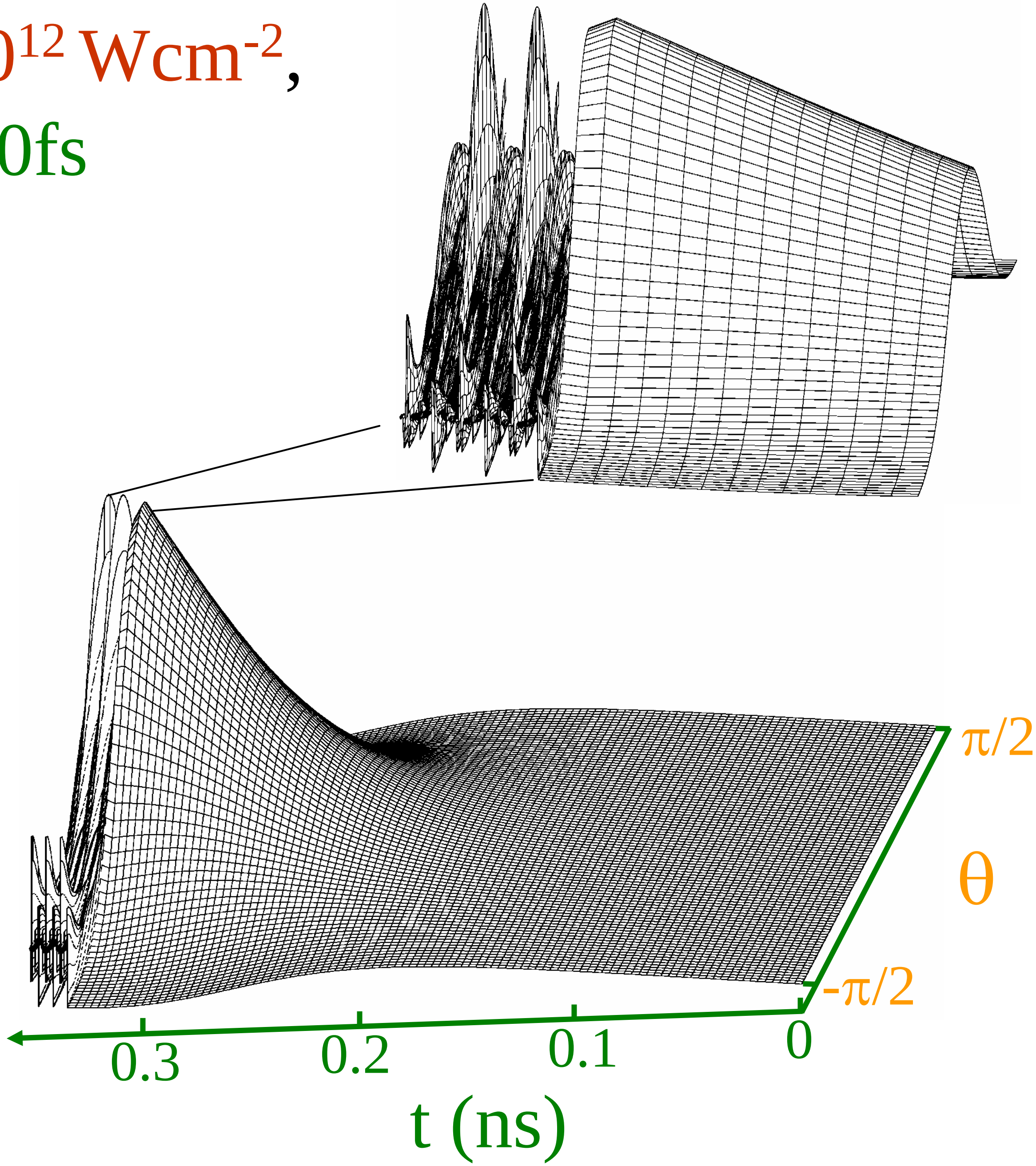
is phased to make an aligned state.



$\tau \gg \tau_{rot}$
DC limit
$B_e \Omega_R \tau^2 < \mathbf{1}$
Post-pulse alignment enhancement
$\tau \ll \tau_{rot}$
$\tau_{on} \gg \tau_{rot}$
$\tau_{off} \ll \tau_{rot}$

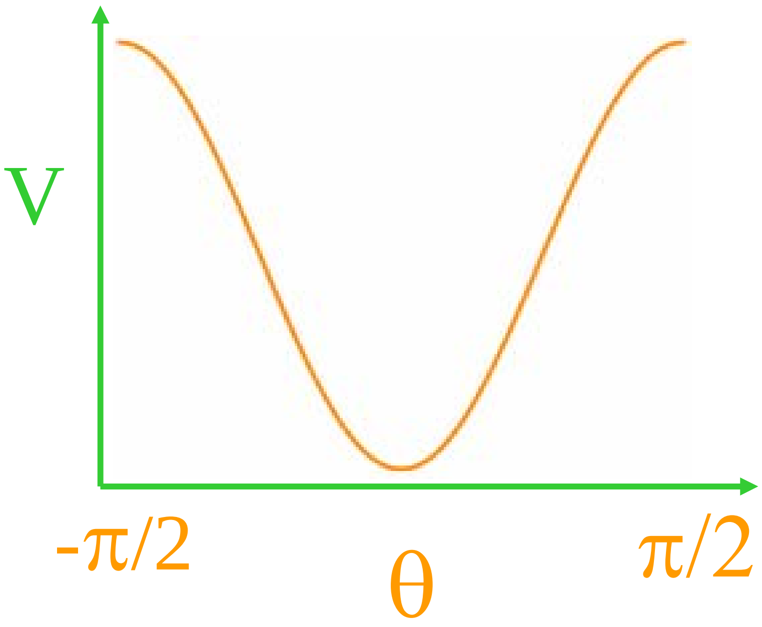
e.g., Cl_2, 3K, 6×10^{12} Wcm^{-2},

τ_{on}=700ps, τ_{off}=100fs

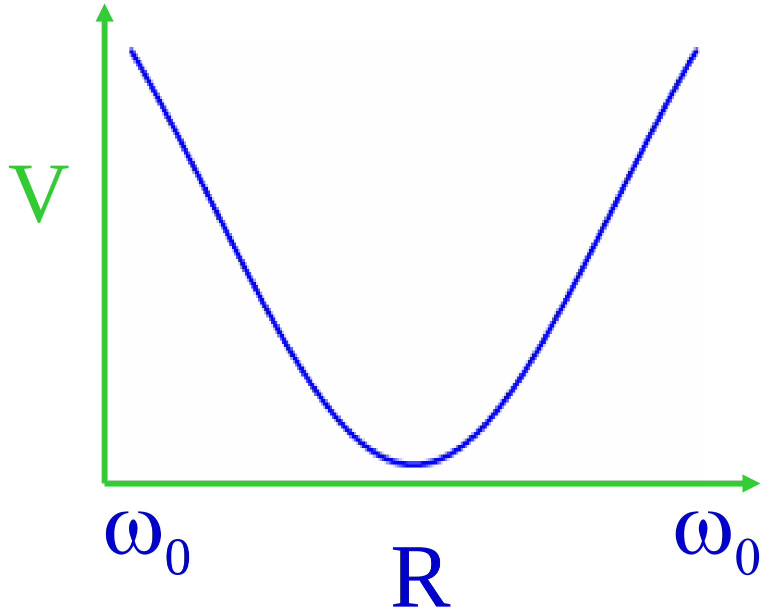


Z.C. Yan & T.S. J.Chem.Phys. 111, 4113 (1999)

$$-\frac{dV}{d\theta} = \text{useful torque}$$

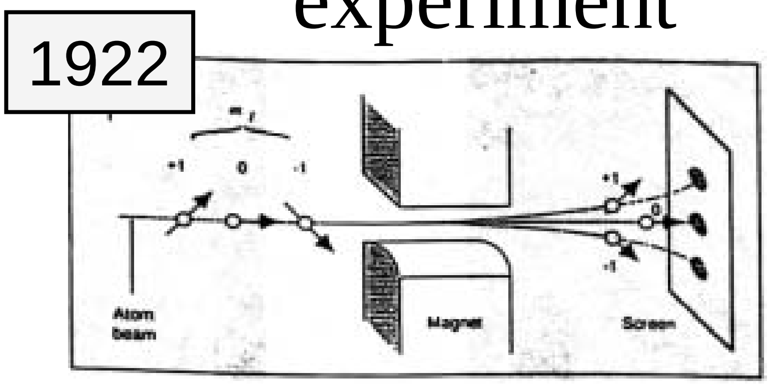


$$-\frac{dV}{dR} = \text{useful force}$$

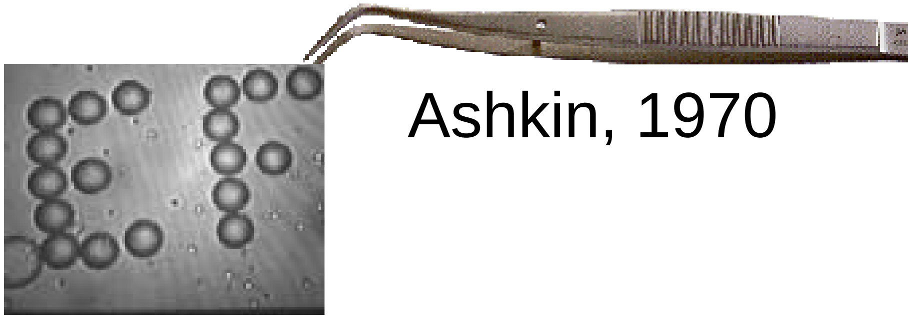


The qualitative physics is very general

•The Stern-Gerlach experiment

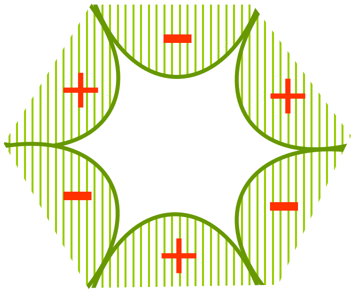


•Optical tweezers



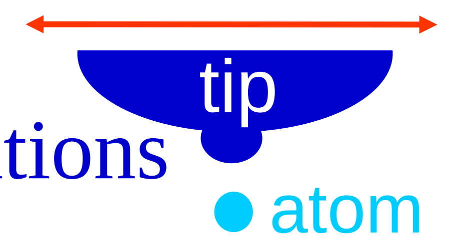
Ashkin, 1970

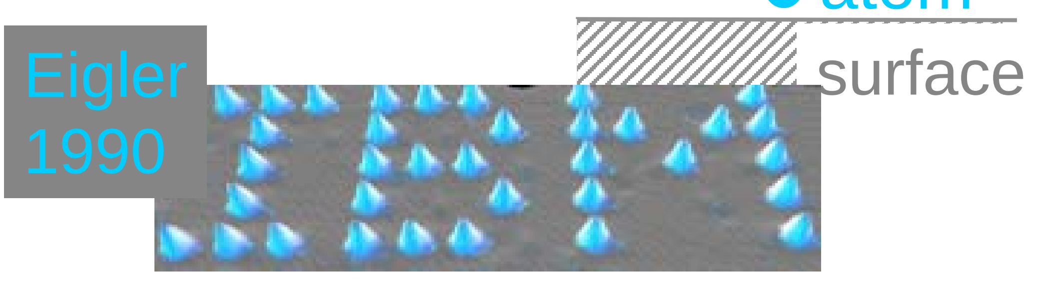
•Hexapole focusing

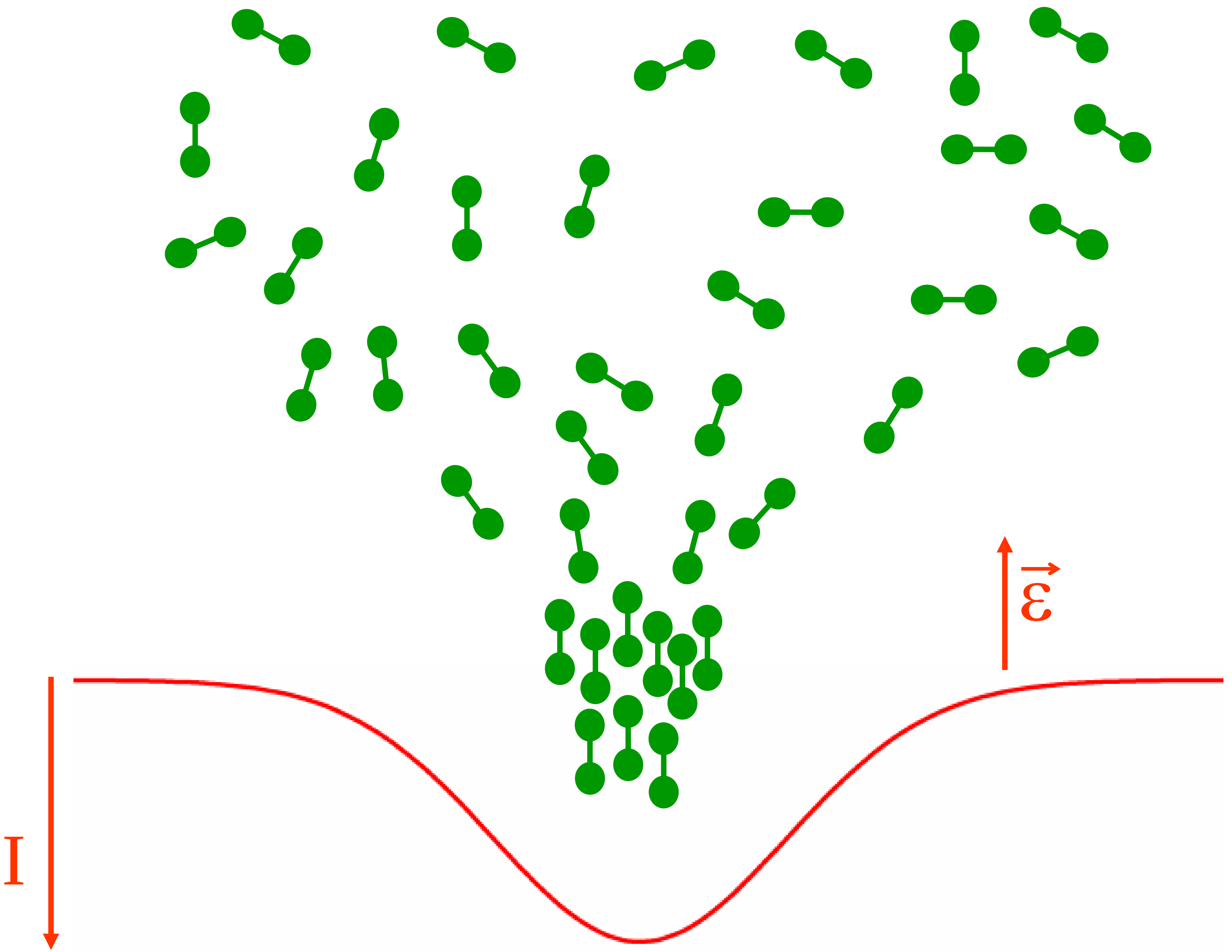


Bernstein 1965

•STM manipulations



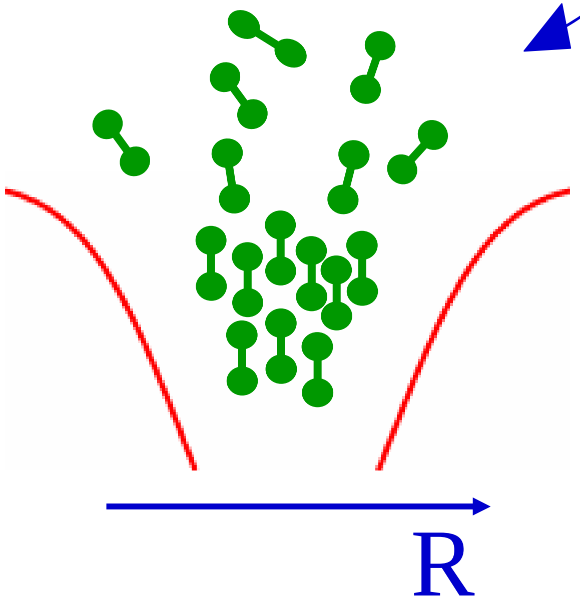


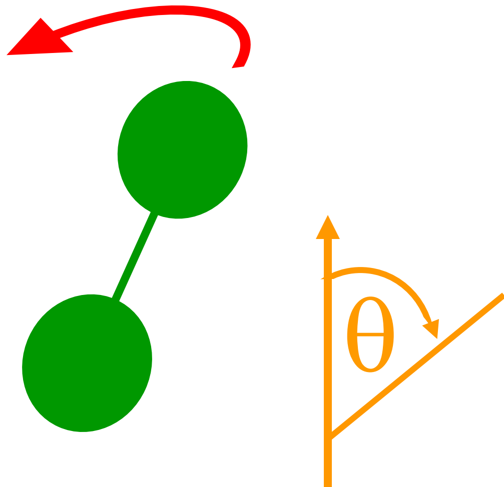


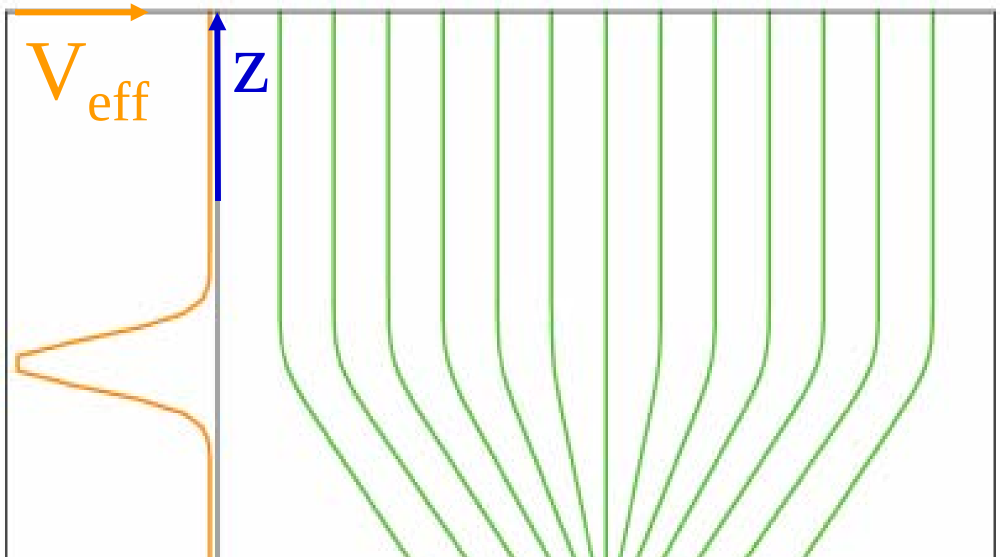
$\vec{\varepsilon}$
I

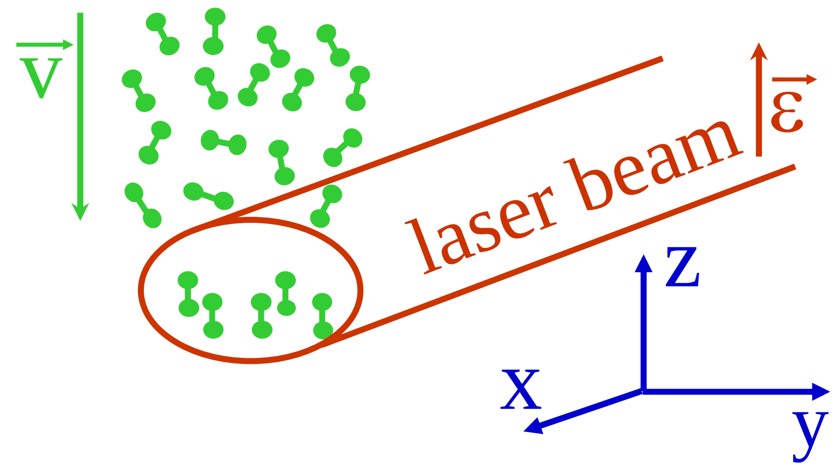
e.g., linear molecule, linear polarization

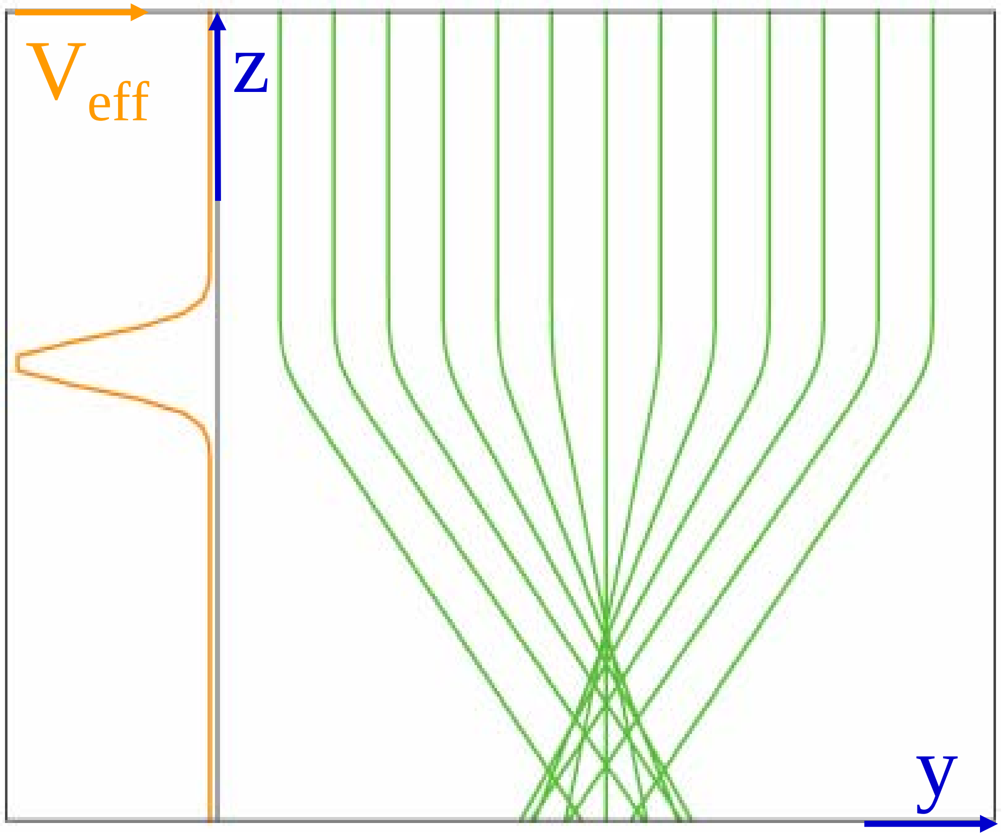
$$V = -\frac{1}{4}\,\varepsilon_0^{\,2}\,\exp(-R^2/\omega_0^{\,2})\,[\,\Delta\alpha\cos^2\theta + \alpha_\perp]$$

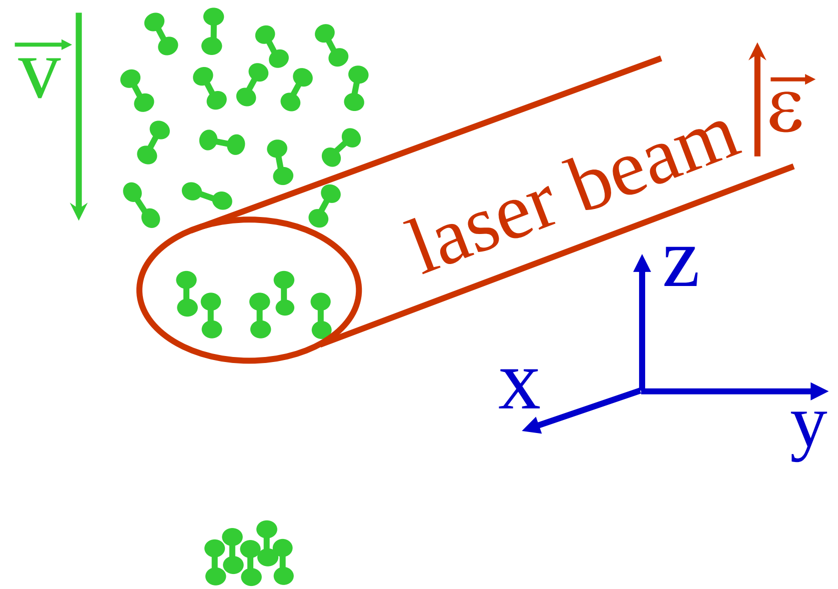




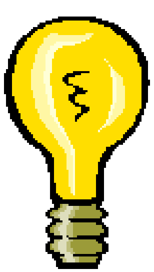

V
eff
z

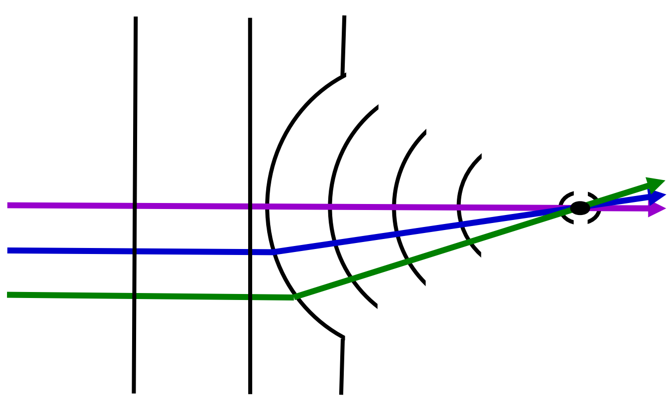

v
laser beam
ε
z
x
y



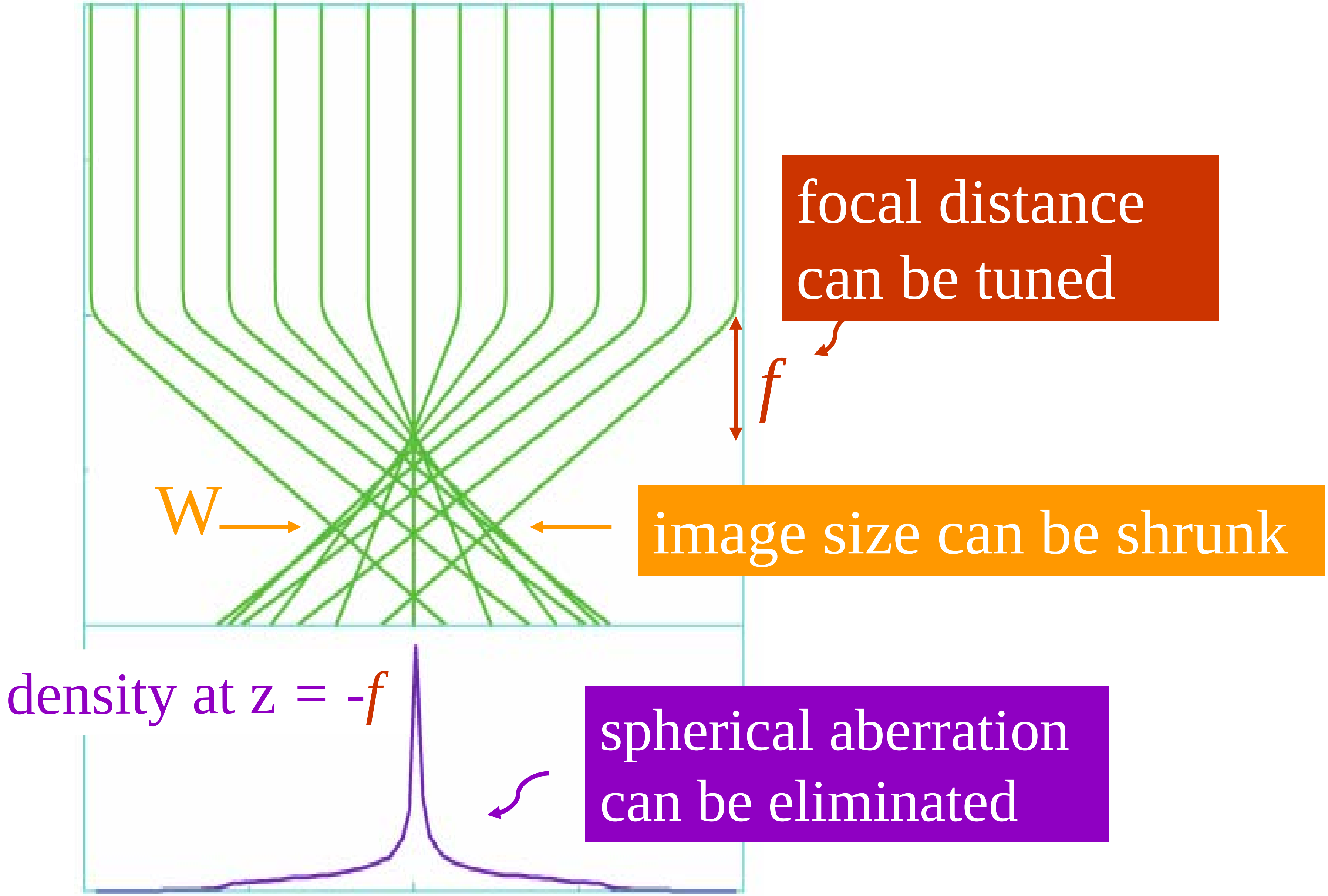


The laser beam serves as a focusing lens...





T.S., Phys.Rev.A **56**, R17 (1997)



T.S., J.Chem.Phys. **106**, 2881 (1997)

JOURNAL OF CHEMICAL PHYSICS VOLUME 114, NUMBER 19 15 MAY 2001

Molecular lens applied to benzene and carbon disulfide molecular beams

Hoi Sung Chung, Bum Suk Zhao, Sung Hyup Lee, Sungu Hwang, Keunchang Cho, Sang-Hee Shim, and Soon-Mi Lim
School of Chemistry, Seoul National University, Seoul 151-747, Korea

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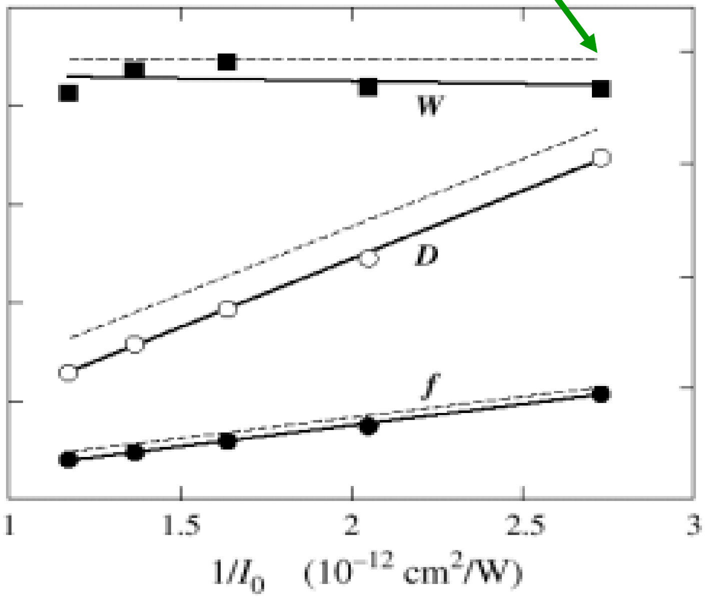
Department of Chemistry, Soongsil University, Seoul 156-743, Korea

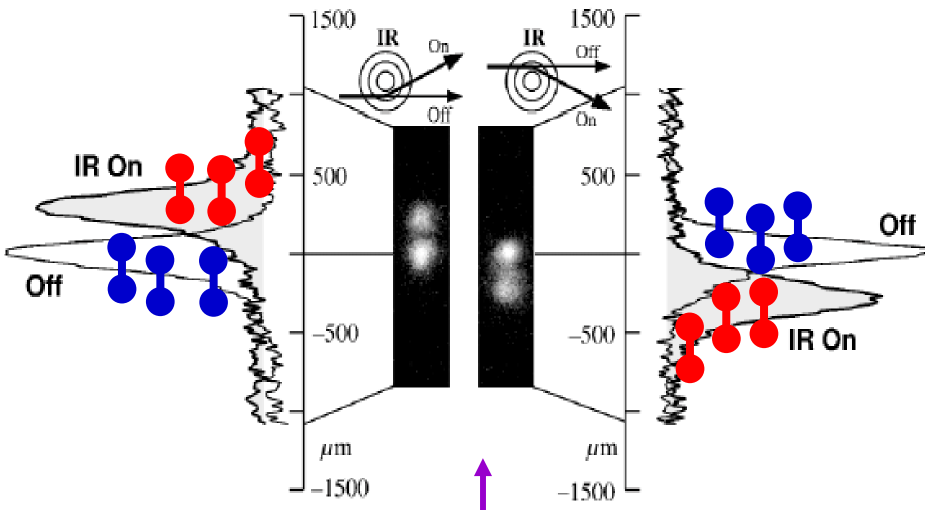
Doo Soo Chung[a)]
School of Chemistry, Seoul National University, Seoul 151-747, Korea

Earlier experimental realizations are reported in:

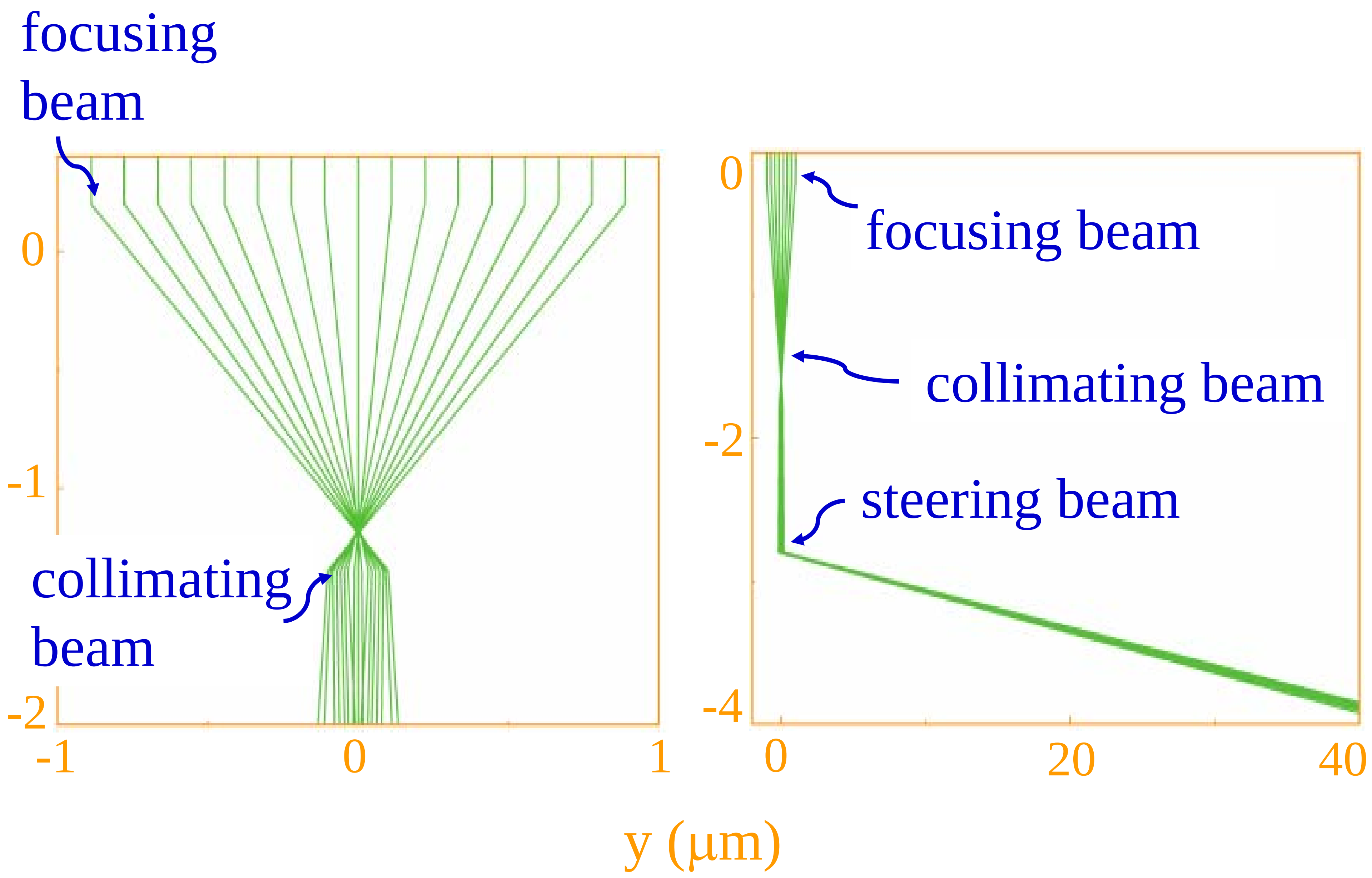
- PRL **79**, 2787 (1998)
- PRA **57**, 2794 (1998)
- PRL **85**, 2705 (2000)

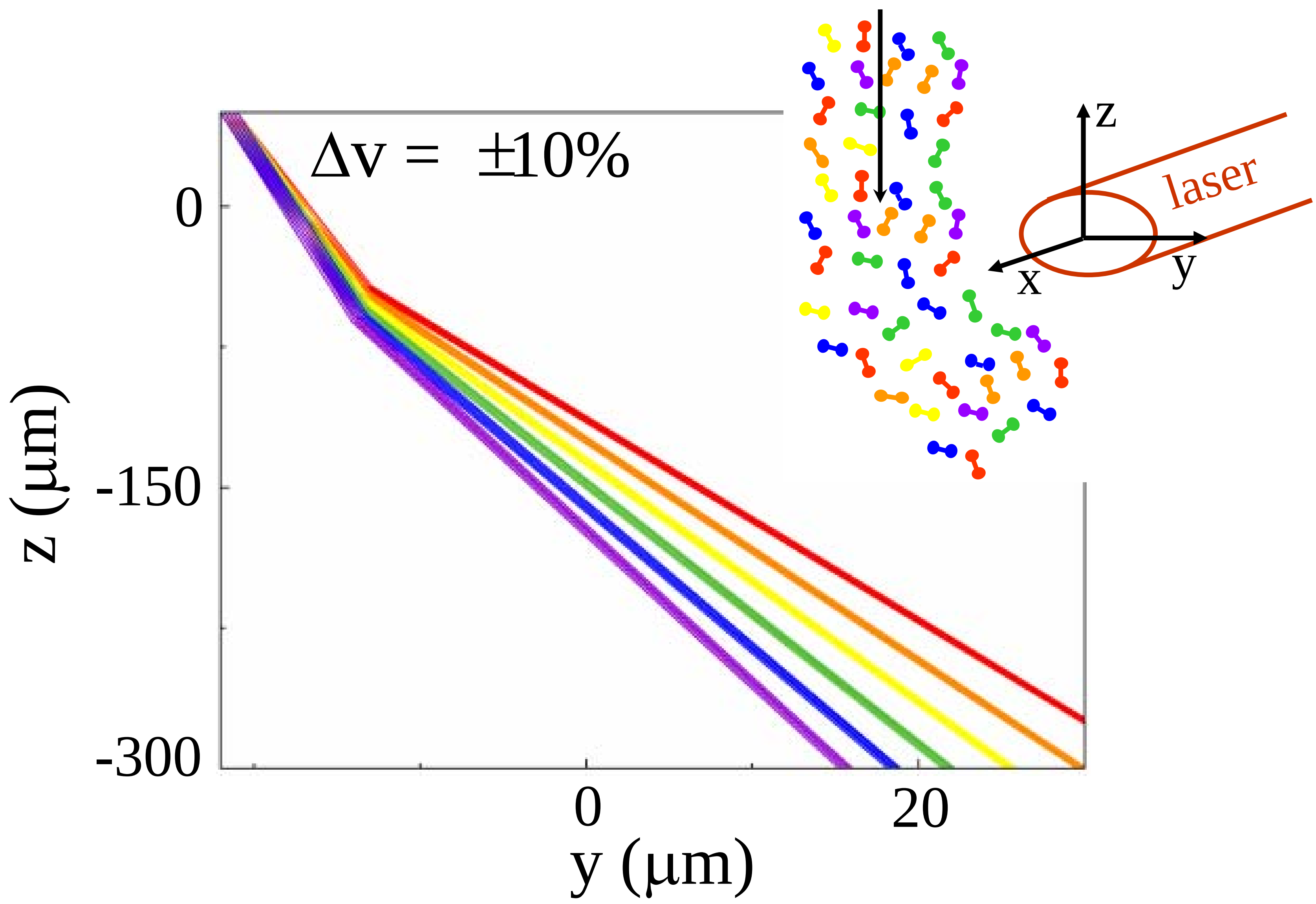
Lens parameters as defined in J.Chem.Phys. **106**, 1881 (1997)



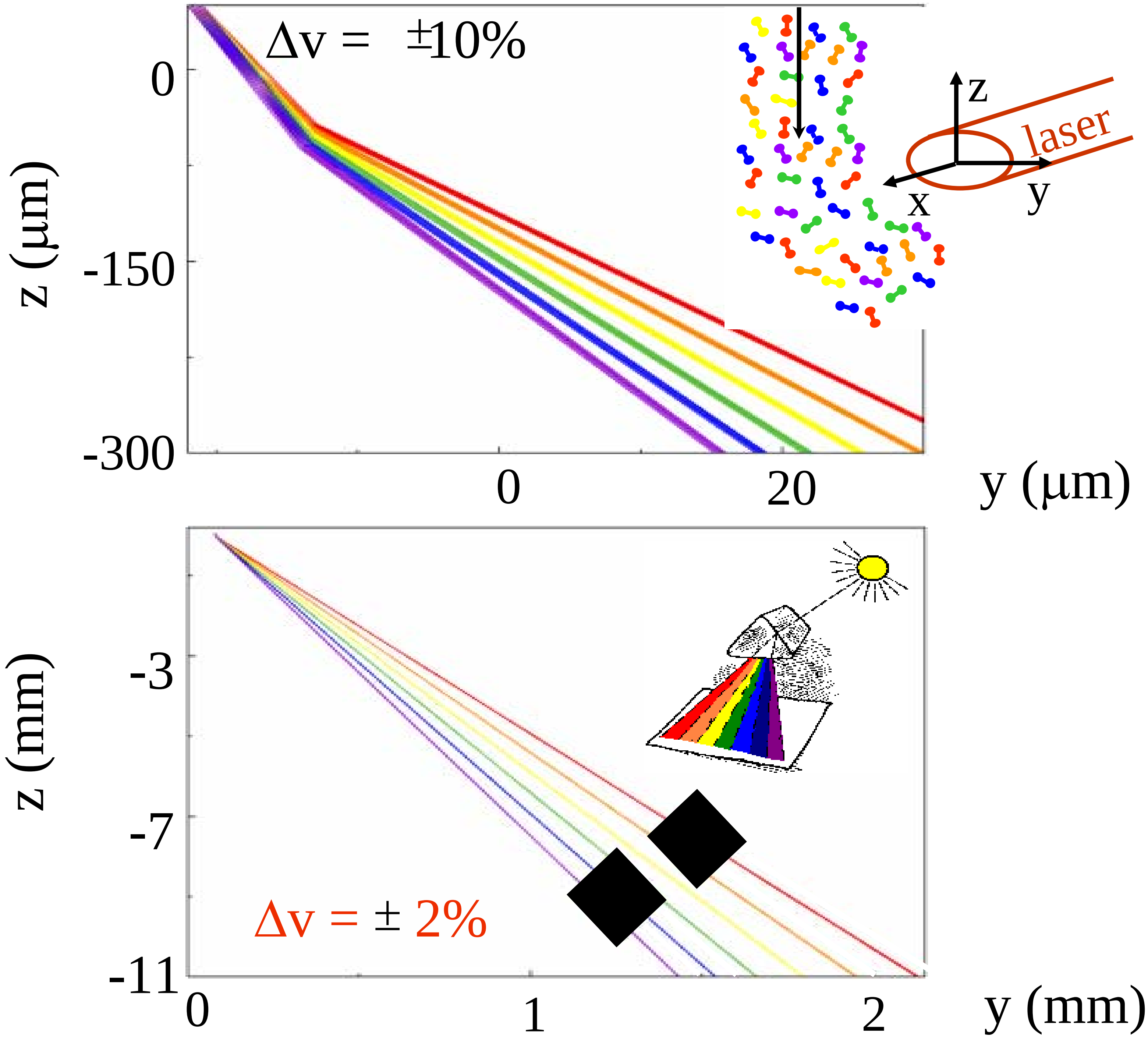


Velocity-mapped ion images and profiles for the deflected and undeflected molecules


focusing beam
collimating beam
focusing beam
collimating beam
steering beam
0
-1
-2
-1
0
1
0
-2
-4
0
20
40
y (μm)

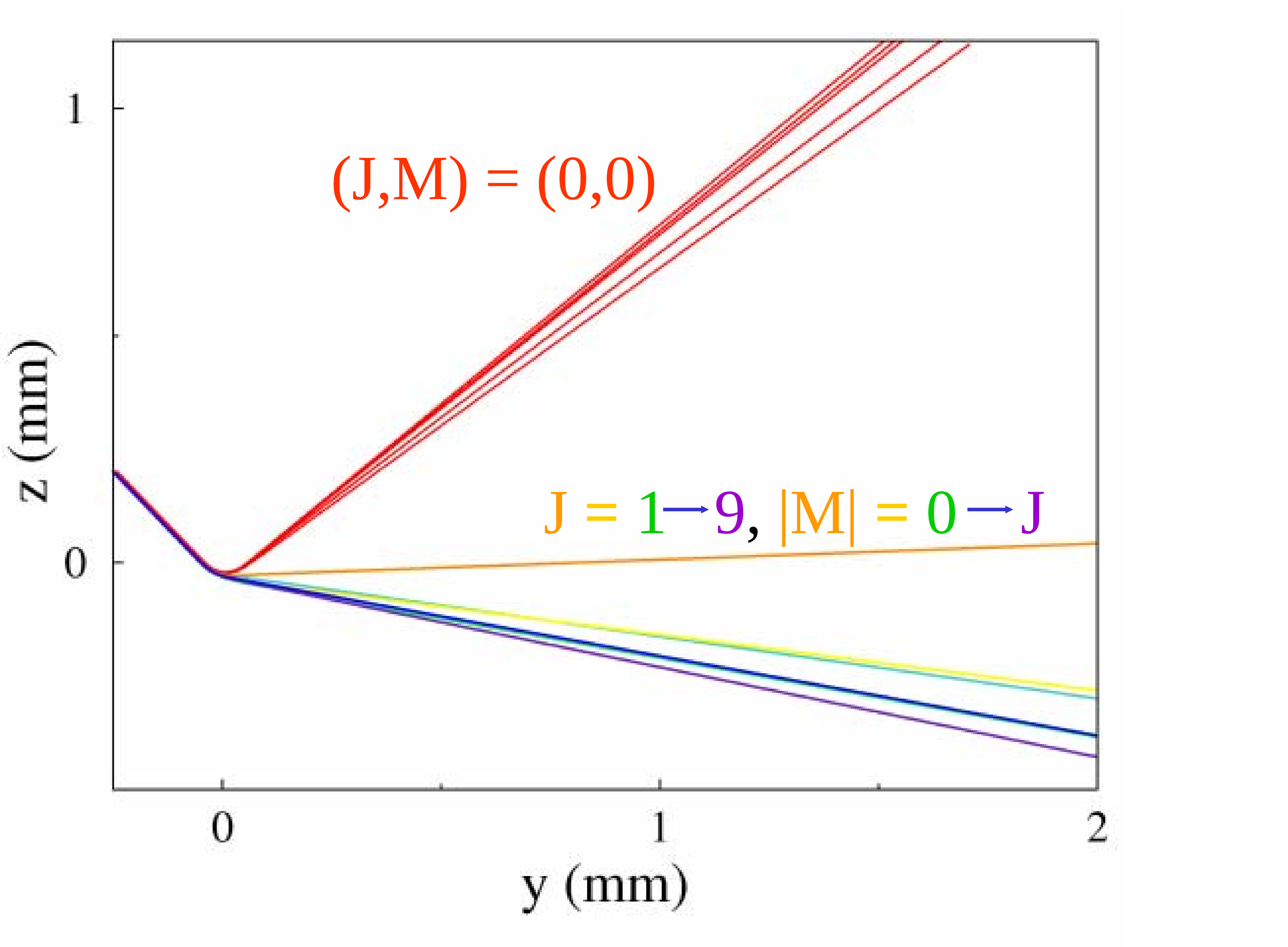


Δv = ±10%
0
-150
-300
z (μm)
0
20
y (μm)
z
laser
x
y

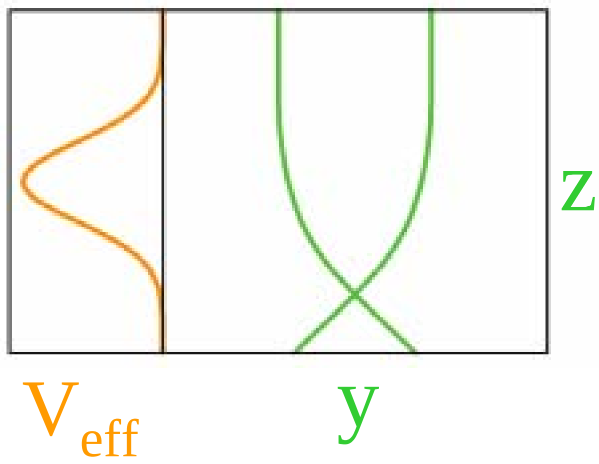


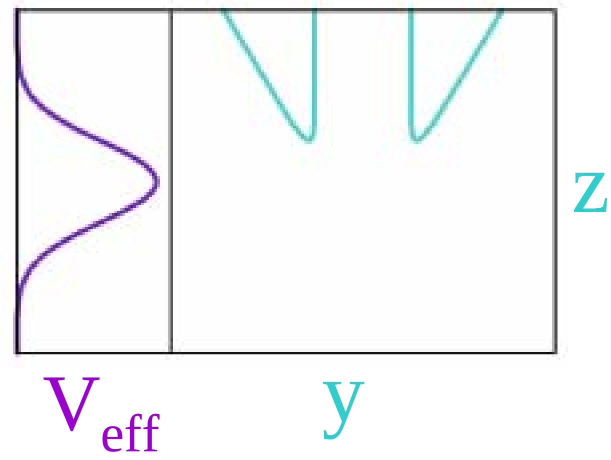
Δv = ±10%
z (μm)
0
-150
-300
0
20
y (μm)
z
laser
x
y
z (mm)
-3
-7
-11
0
1
2
y (mm)
Δv = ± 2%

Li$_2$, 10 K

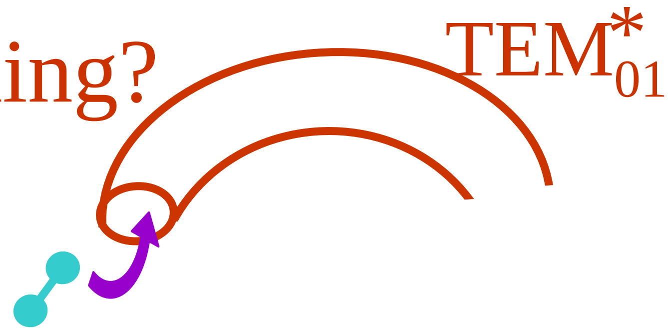


Repulsive Molecular Optics Elements



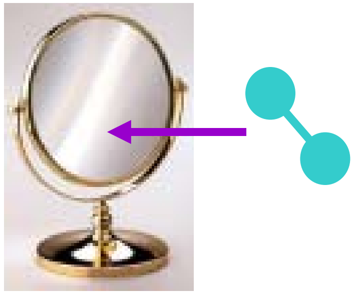


- Waveguiding?

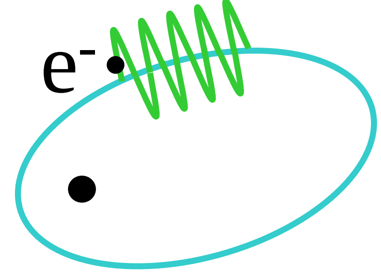


- Trapping?

- Hard-wall collisions?

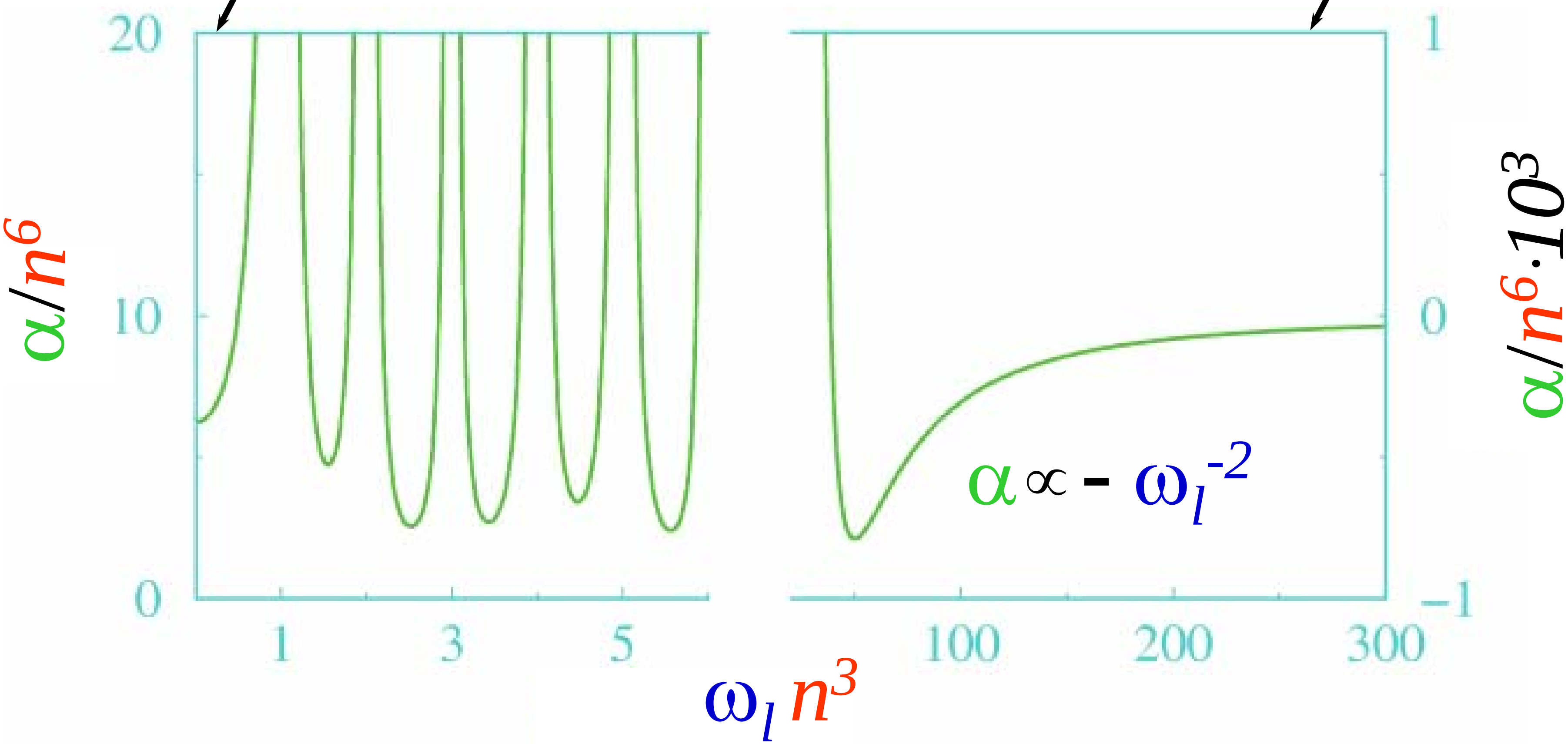


$\omega_e \sim n^{-3} \ll \omega_l$



e.g., $\left\{ \begin{array}{l} n \sim 100, \\ \omega_l \sim \text{microwave} \end{array} \right.$

e.g., $\left\{ \begin{array}{l} n \sim 100, \\ \omega_l \sim \text{IR} \end{array} \right.$

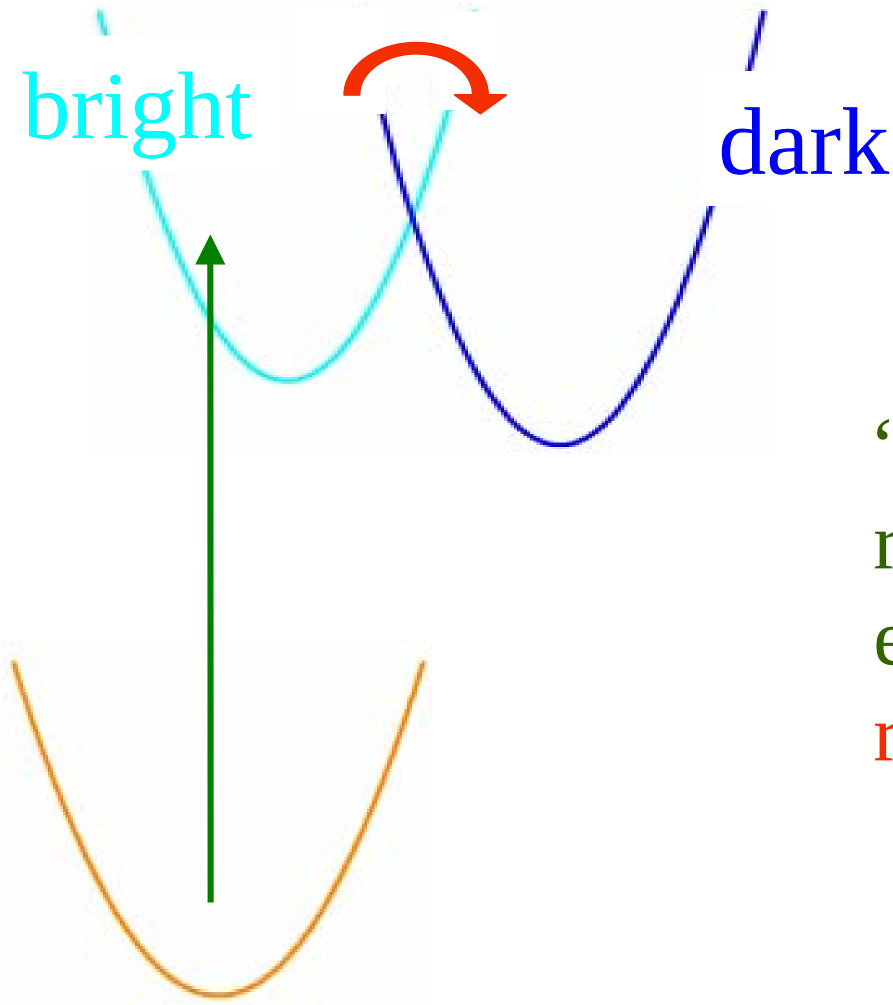


T.S., J.Chem.Phys. **111**, 4397 (1999)

What's it good for ?

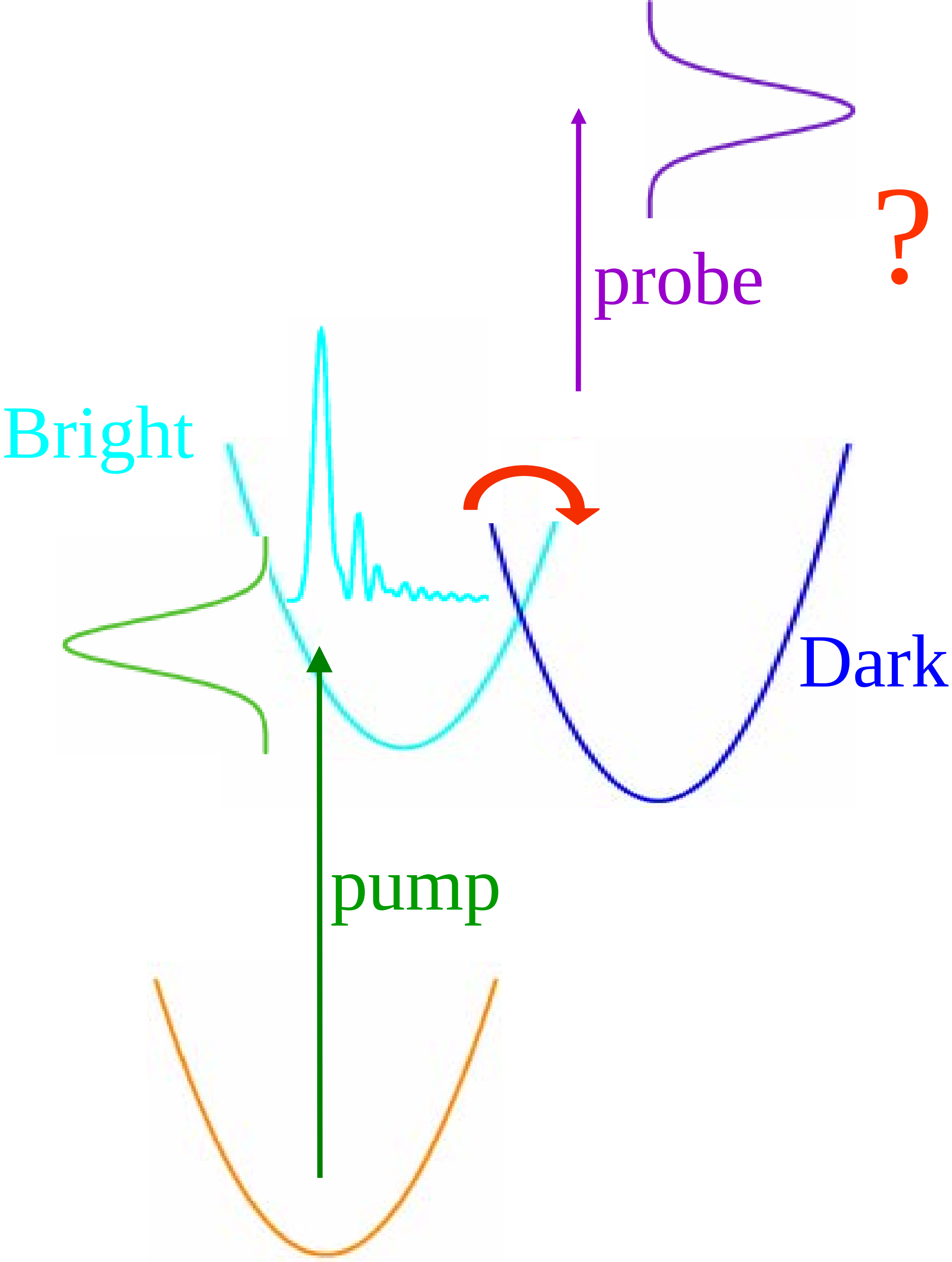
- Alignment as a means of enhancing the sensitivity of pump-probe signals
- Simultaneous molecular alignment and molecular optics as a route to nanoscale deposition and etching
- Adiabatic alignment as a tool in high harmonic generation
- Control of photodissociation branching ratios
- Pulse-pulse alignment as a route to attosecond pulses
- Light-controlled molecular switches

1) Time domain probes of Radiationless Transitions



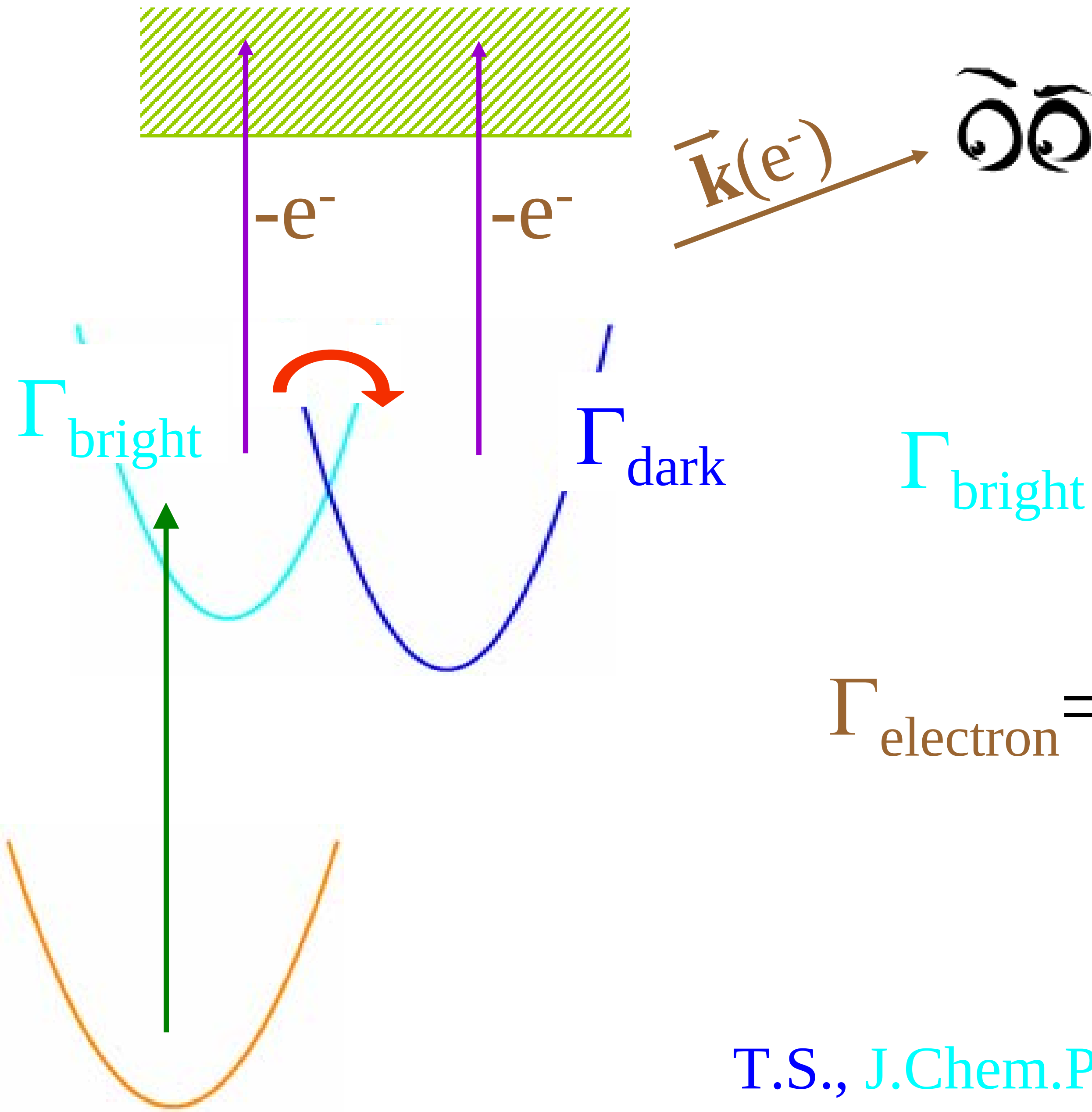
"All photochemical reactions depend on the existence of one or more radiationless transitions"

Jortner, Rice & Hochstrasser, 1969



•Kim *et al* JCP
103, 6903 (1995)
•Radloff *et al* CPL
281, 20 (1997)
•Blanchet *et al* Nature
401, 52 (1999)

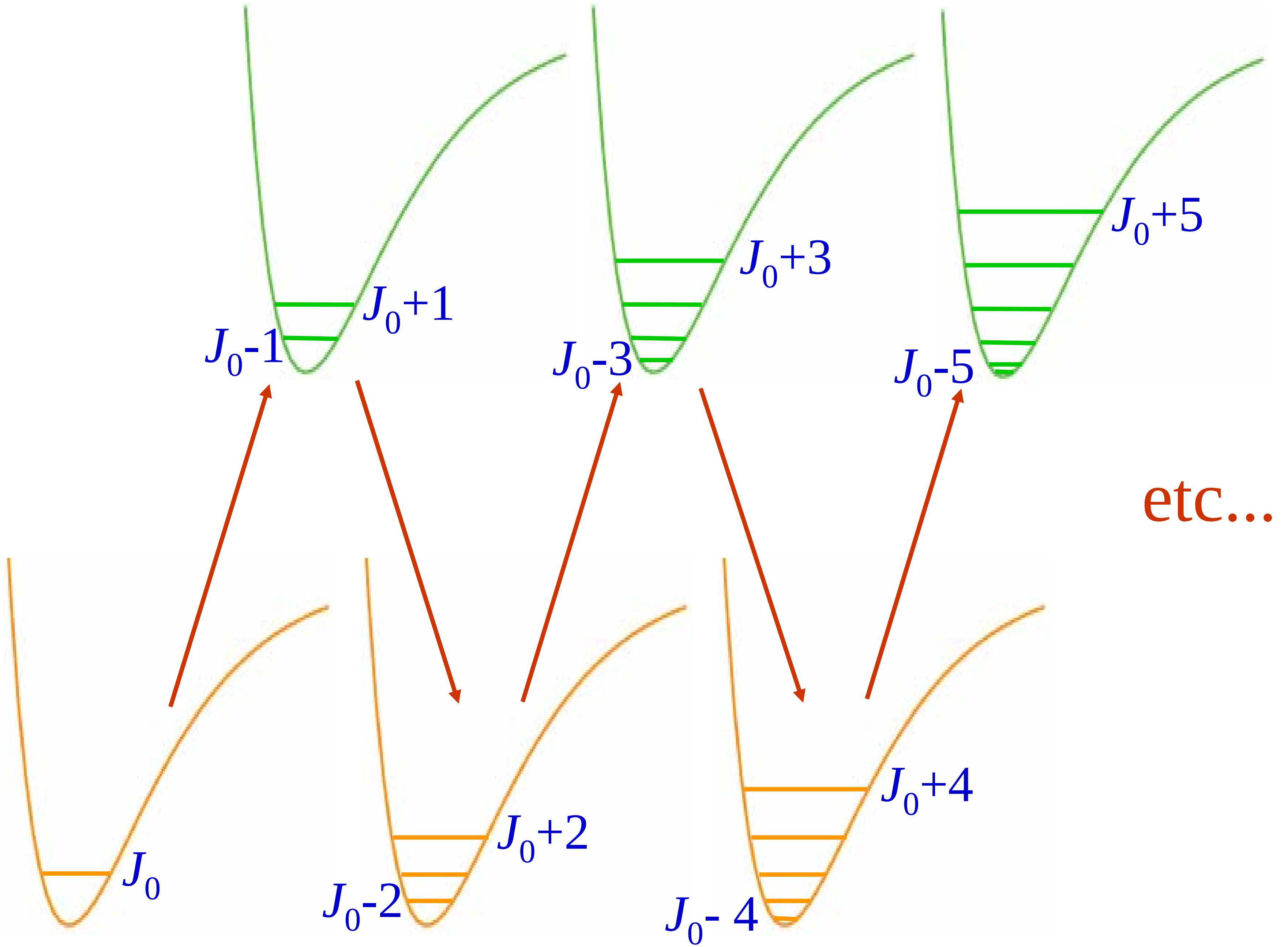
$$\Gamma_{electron} = \Gamma_{neutral} \otimes \Gamma_{probe} \otimes \Gamma_{ion}$$



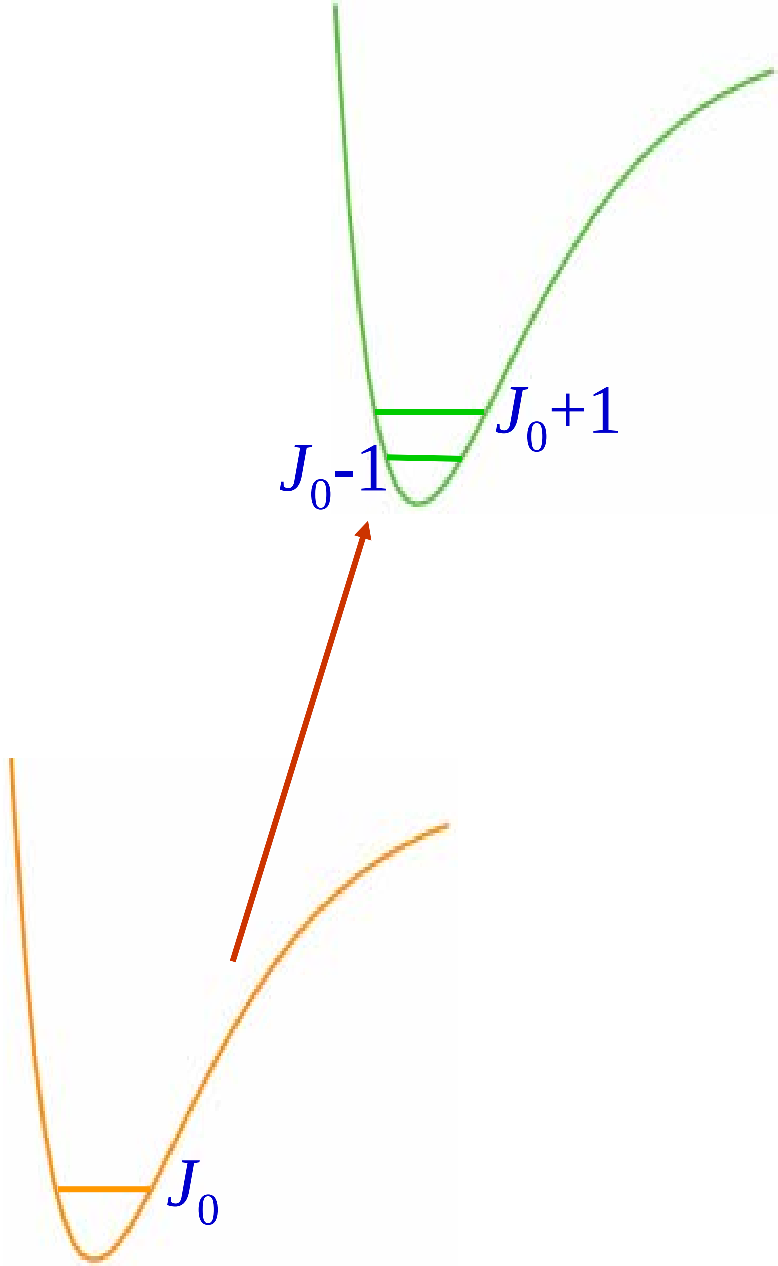
$$\Gamma_{bright} \neq \Gamma_{dark}$$

$$\Gamma_{electron} = \Gamma_{electron}(\Delta t)$$

T.S., J.Chem.Phys. **113**, 1677 (2000)



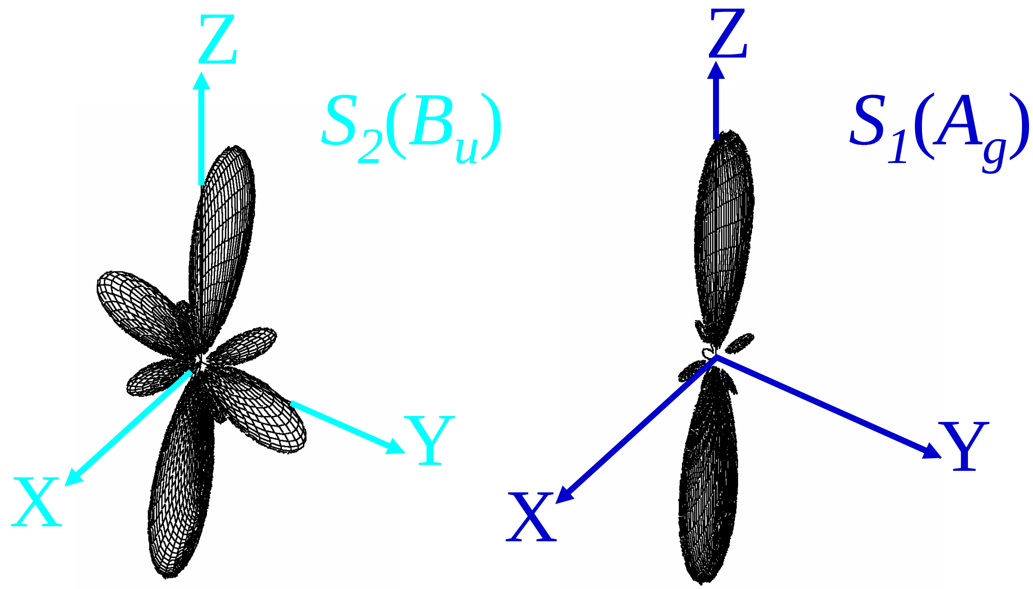
J_0-1
J_0+1
J_0-3
J_0+3
J_0-5
J_0+5
etc...
J_0
J_0-2
J_0+2
J_0- 4
J_0+4



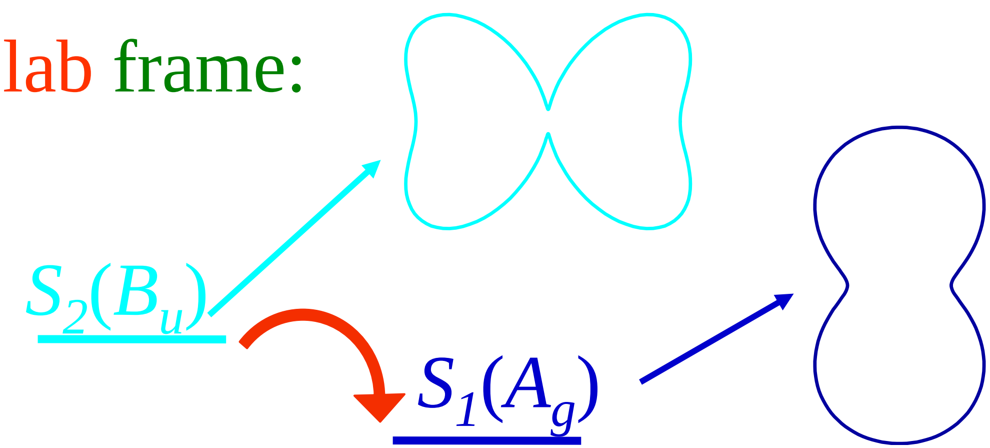
J_0+1
J_0-1
J_0

Consider, e.g., the internal conversion of a linear polyene:

In the molecular frame:

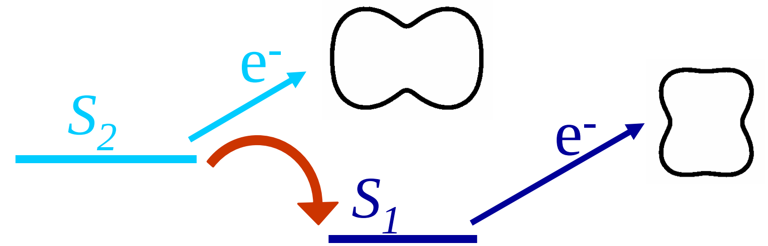


In the lab frame:

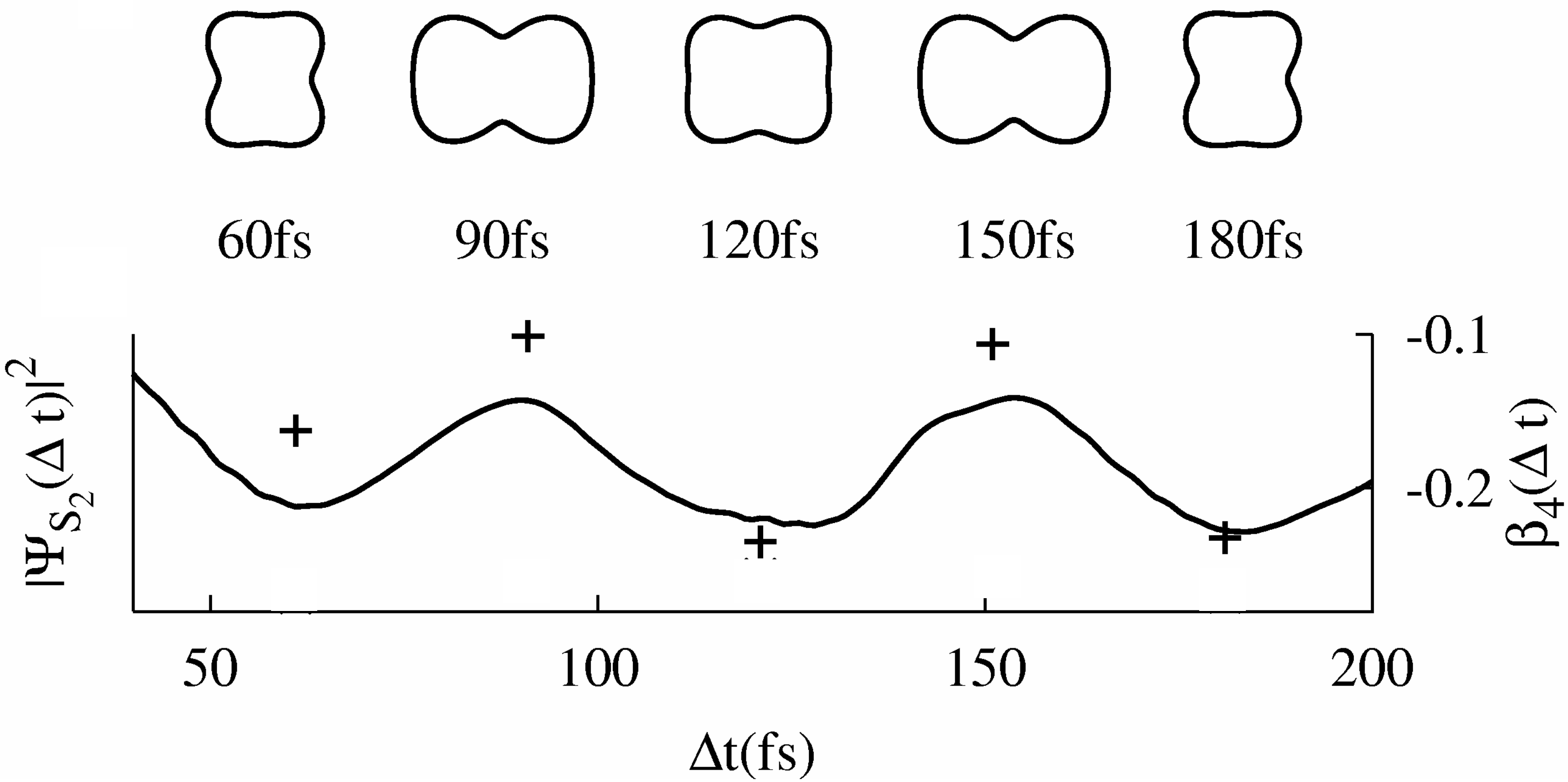


T.S., J.Chem.Phys. **113**, 1677 (2000)

It gets more exciting in the strong pulse case



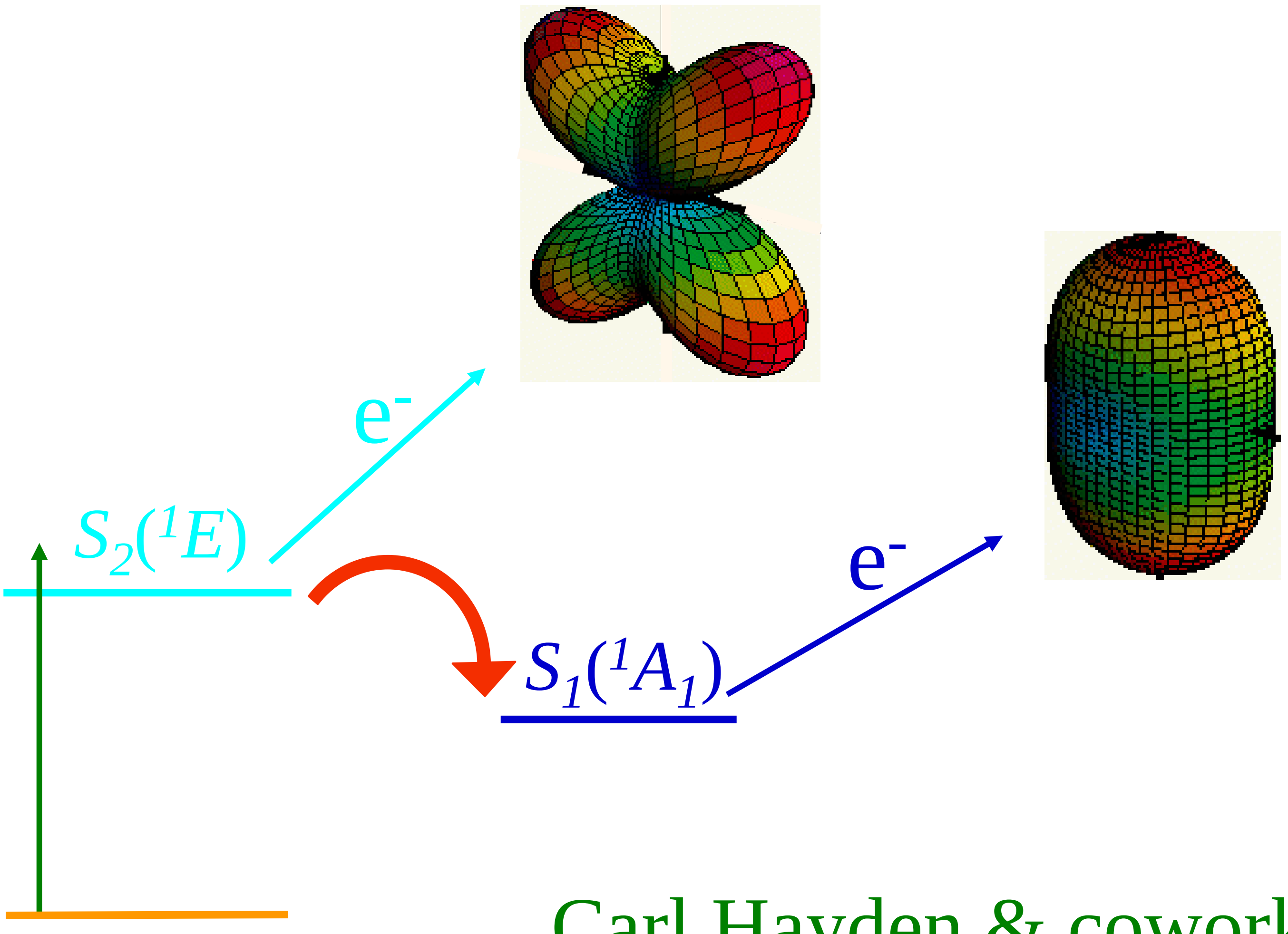
e.g., the internal conversion of pyrazine



Y.-I. Suzuki, M. Stener & T.S.,
Phys.Rev.Lett. **89** 233002 (2002)

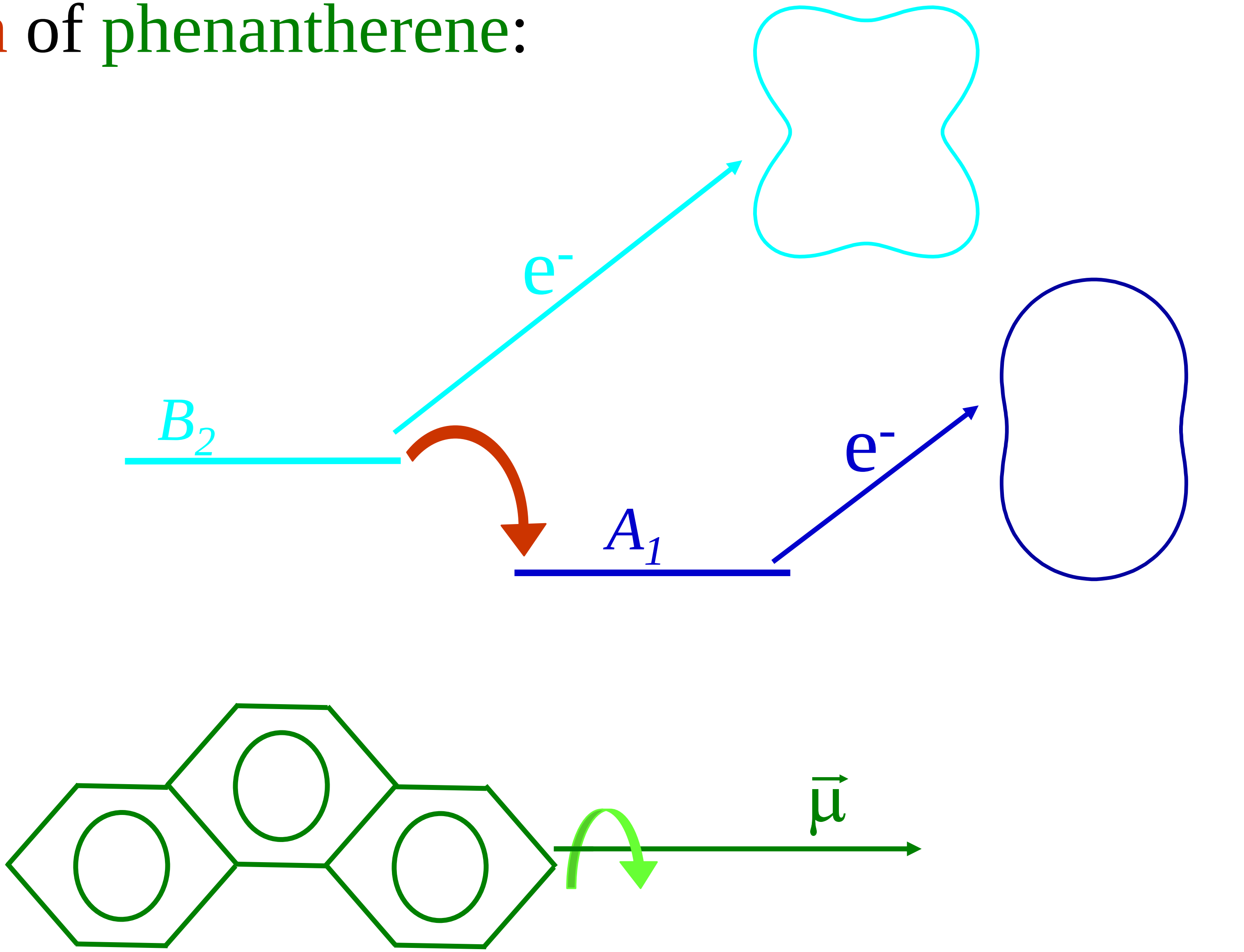
A first experimental realization:

Time-resolved photoelectron angular distributions from DABCO



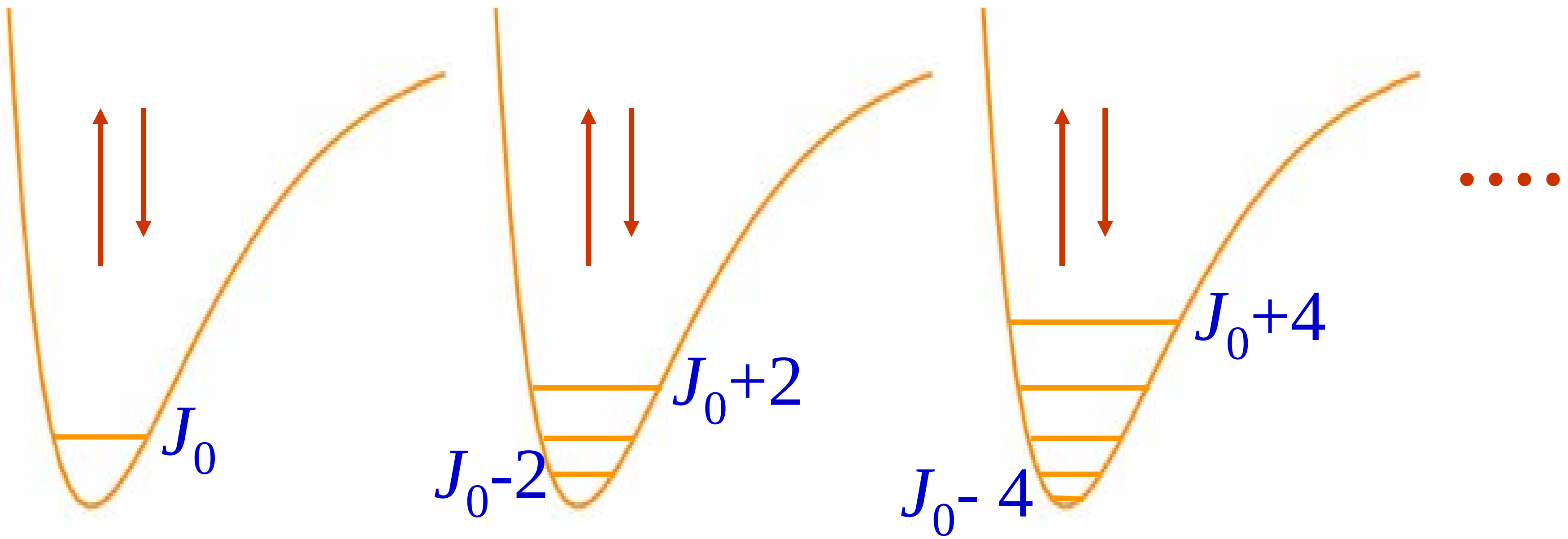
Carl Hayden & coworkers, a very beautiful experiment (unpublished)

Consider, by contrast, the internal conversion of phenantherene:

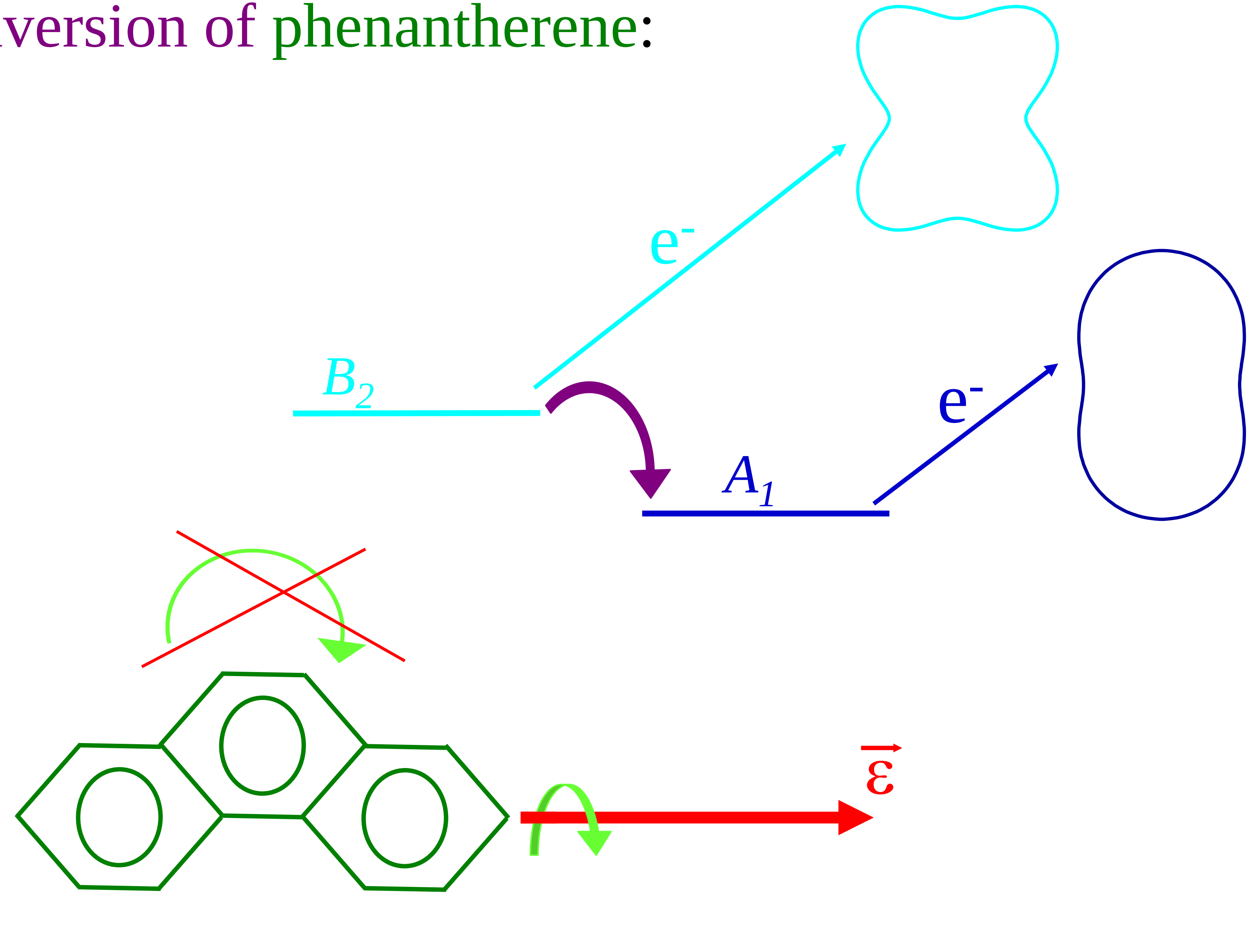


The pump-induced alignment does not do the job

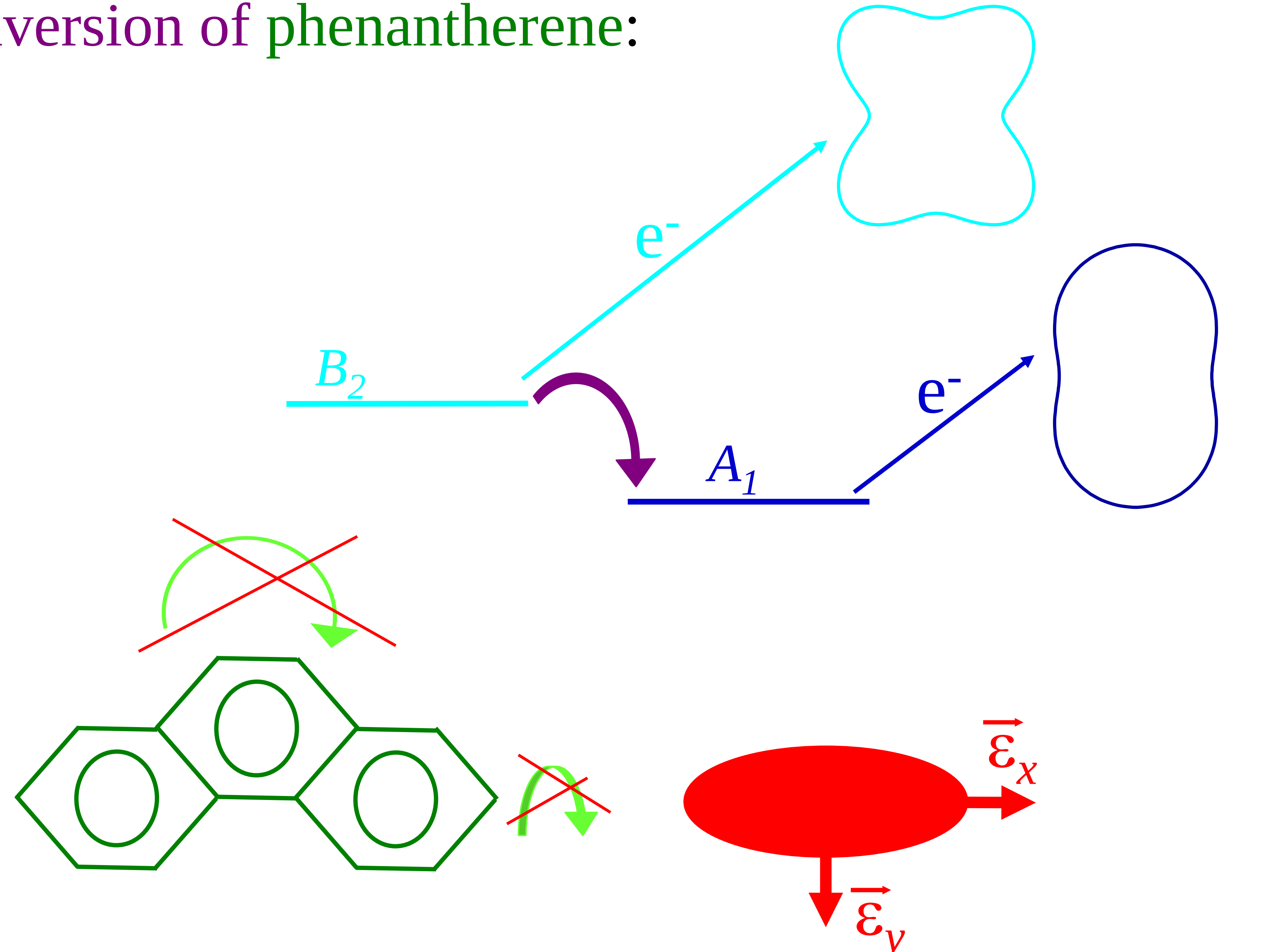
At nonresonant frequencies ($\omega \ll \omega_{elect}$) rotational excitation takes place via two-photon cycles



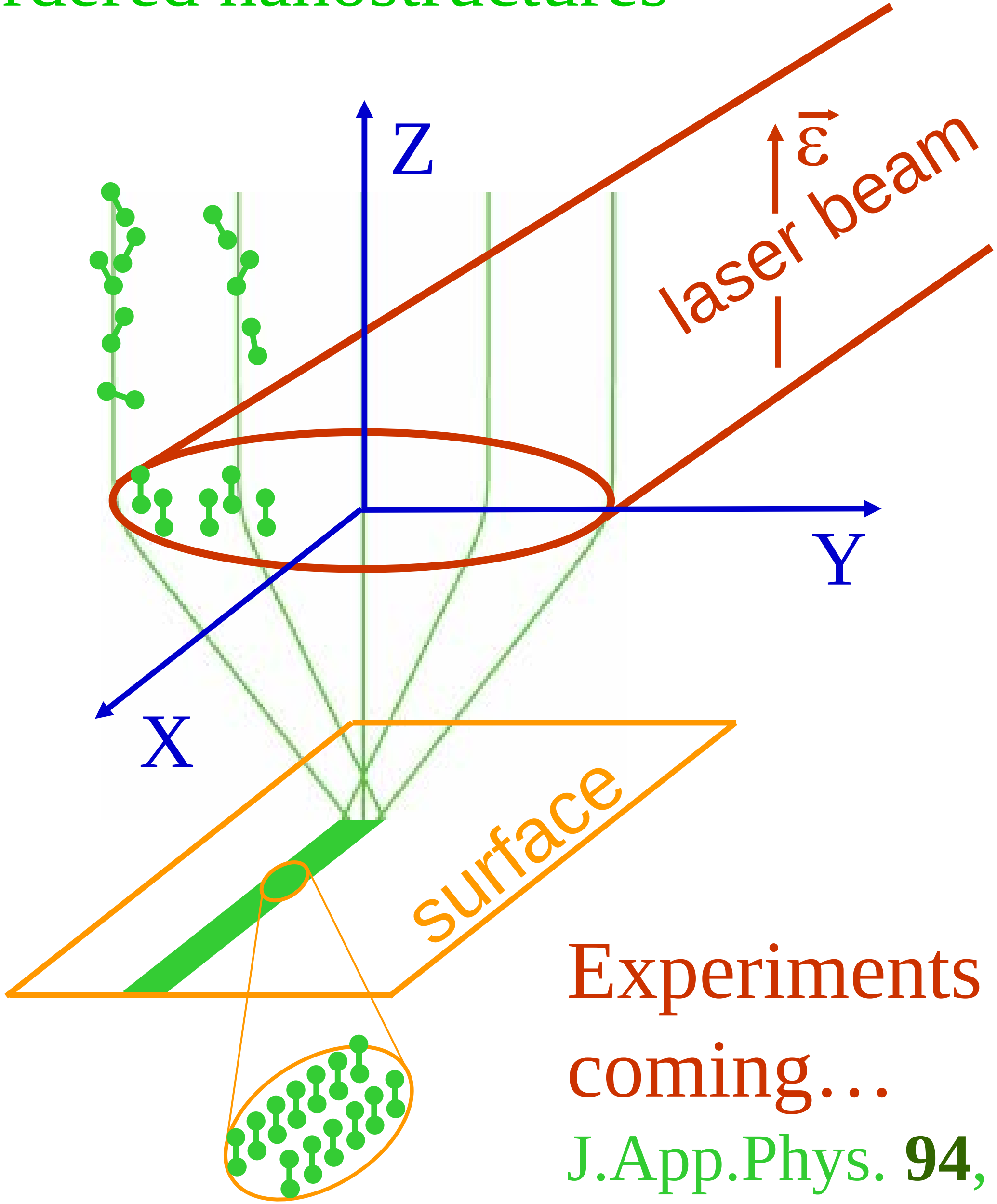
Consider again the internal conversion of phenantherene:



Consider again the internal conversion of phenanthrene:



2) Laser focusing & alignment as a route to orientationally-ordered nanostructures

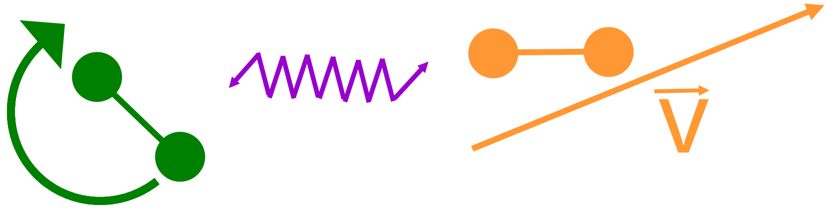


T.S., Phys.Rev. A **56**, R17 (1997)

Experiments are coming…

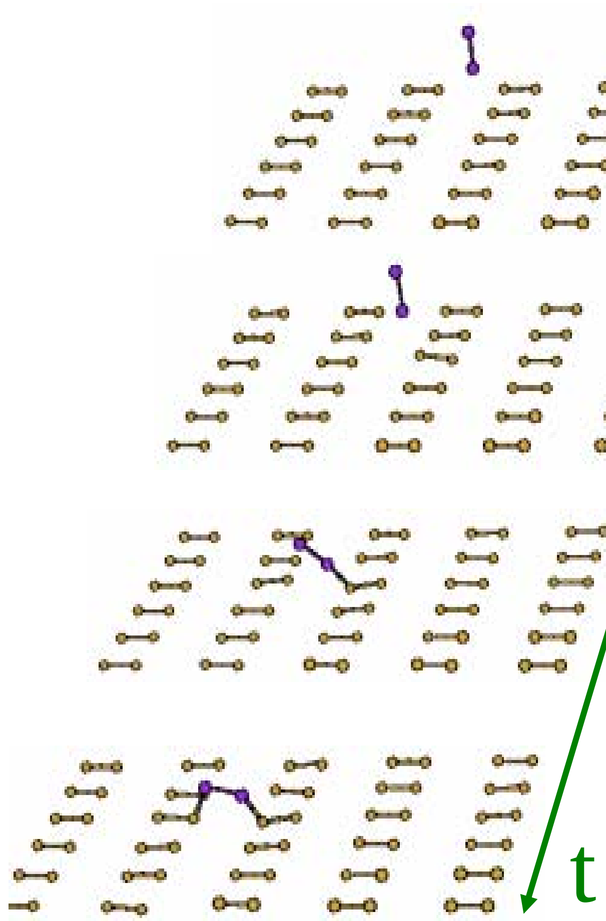
J.App.Phys. **94**, 669 (2003)

•Field-free alignment relies on nonadiabatic turn-off, hence rotation-translation coupling



Z.-C. Yan & T.S., J.Chem.Phys. **111**, 4113 (1999)

•Would the alignment control the surface reaction or vice versa?



D. Sheerinova, A. Lee, S. Bennett & T.S., to be submitted

3) Adiabatic alignment as a tool in high harmonic generation [Phys.Rev.Lett. **87**, 183901 (2001)]

4) 3D adiabatic alignment as a route to control of photodissociation branching ratios [Phys.Rev.Lett. **83**, 1123 (1999)]

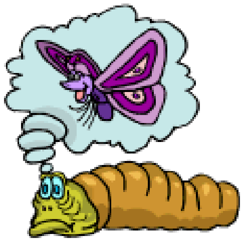
5) Post-pulse alignment as a means of producing attosecond pulses [Phys.Rev.Lett. **88**, 013903 (2002)]

6) Strong field alignment as a route to new forms of electron diffraction [Phys.Rev.Lett. **91**, 203004 (2003)]

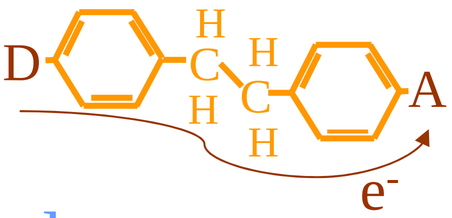
7) Time-periodic alignment as a tool in stereodynamics

But the really exciting applications should be in the dynamics of large molecules & in condensed phases

Few of my favorite dreams…



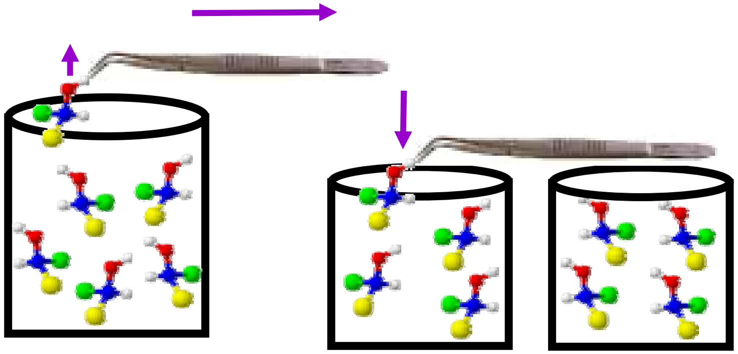
- Combining elliptical polarization with nonadiabatic turn-off to control charge trasfer reactions



- From a gas phase into a condensed matter tool: Alignment & optics in superfluid He

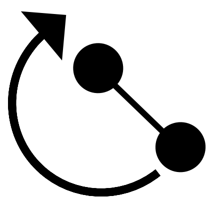
- Pasteur tweezers:

Strong laser alignment as a route separating racemic mixtures into enantiomers (?)



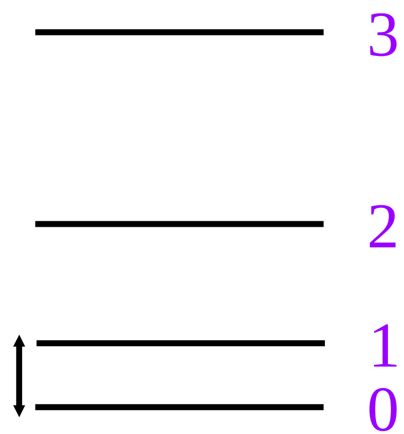
Epilogue

Rotational spectra are a delightful playground for lovers of wavepacket phenomena & angular momentum algebra:



$\Delta J \propto J$

ΔJ = small



- Molecular alignment
- Enhanced alignment after the turn-off
- Three-dimensional alignment
- Molecular focussing
- Molecular mirrors

Thanks to

Former group members:

Zong-Chao Yan
Stuart Althorpe
Yoshi-Ichi Suzuki

Experiments:

Henrik Stapelfeldt & coworkers (Aarhus)

$ NSF CHE/DMR
$ NSF PHY
$ DOE
$ NATO
$ HGF-NRC
$ Guggenheim Foundation
$ Humboldt Foundation

NORTHWESTERN UNIVERSITY